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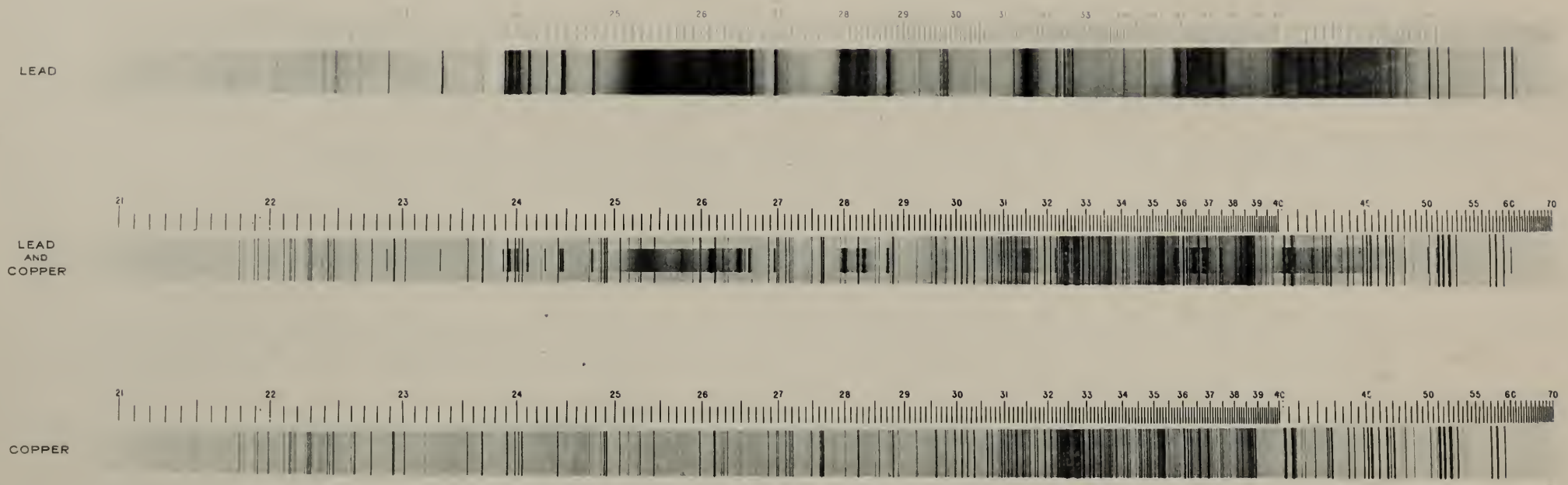

ARC SPECTRA OF LEAD AND COPPER

OPTICAL METHODS

IN CONTROL AND RESEARCH LABORATORIES

BY

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Absorption Spectra
Refractometry
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OPTICAL METHODS IN CONTROL AND RESEARCH LABORATORIES

PREFACE

THE optical methods dealt with in this book are those employing spectroscopes (or spectrographs), spectrophotometers, refractometers, and polarimeters. No detailed descriptions of these instruments or their techniques are included, but in each case references are given to sources of information on these points.

We have already published an essay which deals in a broad and general way with the subject of light radiation in relation to the constitution of matter.[1] There is a tendency to lose sight of the deeper significance of physical properties when they are merely used for the identification of substances and other technical purposes. It is well that such a tendency should be guarded against. In recent physico-chemical investigations the study of optical phenomena is resulting in a great extension of knowledge concerning the intimate structure of the molecule, and must inevitably lead to a commensurately enhanced power of following and controlling the chemical transformations of matter. It was these considerations which made us publish the essay referred to, which although prepared primarily for the interest and stimulation of our staff thus became, we hope, of use to many chemists who had previously lacked time or opportunity themselves to make such a general survey of the subject. But the Works Chemist requires, one may almost say, the maximum of empiricism. To keep pace with his work he needs instruments which he can read at once, and provided with scales giving the percentages he wants, or tables from which he may get the information

[1] *Refractive Index, Absorption, Wavelength, and Rotatory Power in Relation to Molecular Structure*, by Ludwik Silberstein, Ph.D. Adam Hilger, Ltd.

he requires without calculation. Indeed, only if he can hasten the solution of the practical questions which urgently insist on being answered day by day, can he hope to have time to keep in touch with or to carry out research on the fundamental subjects. Such being the needs of the chief market for these types of scientific instruments, we have, in this book, confined ourselves chiefly to practical applications. It is intended as an introduction to the uses of the above instruments, as a guide to their selection, and as an index to further sources of information concerning their employment in control and research laboratories.

SECTION I

METALLURGICAL AND ANALYTICAL APPLICATIONS OF SPECTROSCOPY

ANALYSIS BY EMISSION SPECTRA

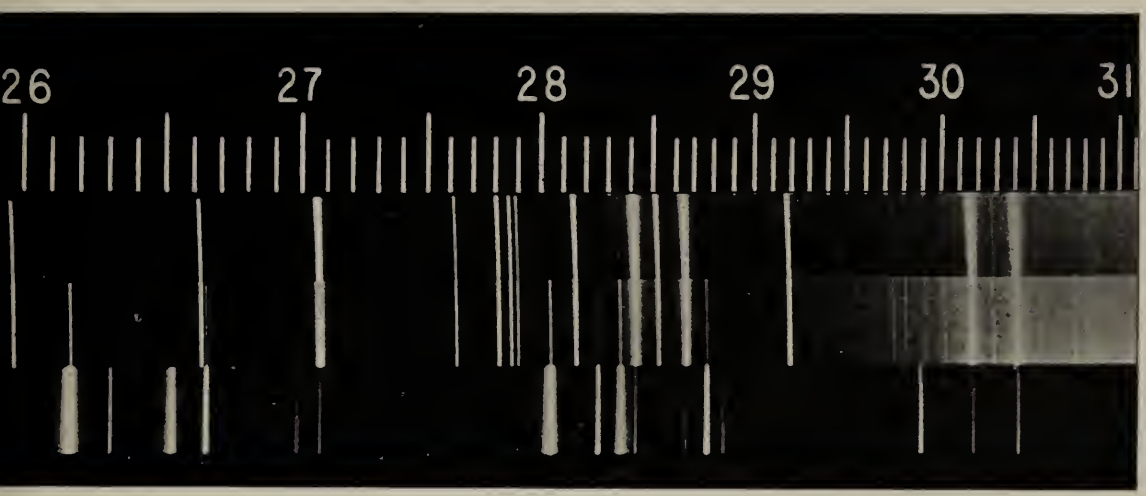


FIG. 2.

Illustrating mode of obtaining comparison spectra by the Hartmann diaphragm supplied with Quartz Spectrographs E 1, E 2, and E 6

INTRODUCTION

THE discoveries of the radioactive elements, of the isotopes, and of the disintegration of elements under radioactive bombardment have made necessary a great change in the notion of the elements, but they have left unshaken the foundations of spectrum analysis. It is still true that the spectrum of a metal establishes its chemical identity.

The isotopes of lead (to take one example) have the same spectrum,[1] but they have also the same chemical properties and are chemically inseparable. The radioactive elements disintegrate into other and chemically different substances, but each of these products exhibits at once its characteristic spectrum.

[1] This statement requires qualification, though not in a sense destructive of the argument. Merton, using interference apparatus made by Adam Hilger, Ltd., has detected minute differences in the spectra of lead from different sources. No chemical differences are yet known to exist between these samples other than those of atomic weight customary with isotopes. *Proc. Roy. Soc.*, A, vol. xcvi. p. 388, 1920, and A, vol. c. p. 84, 1921.

Thus the infallibility of the spectroscope from the chemical point of view is even more firmly established than before.

The use of spectrum analysis in industrial laboratories had until the last ten years made surprisingly little progress since the time of Kirchoff and Bunsen ; but the introduction of the Hilger Wavelength Spectrometers and Quartz Spectrographs and the contemporaneous laboratory work of Leonard and Pollok, A. de Gramont, and others, have provided convenient instruments and established techniques which render prior study of spectroscopy unnecessary, and industrial chemists are now rapidly availing themselves of the saving of time and increased certainty resulting from the use of these facilities.

This section is a brief recital of some of the most interesting of recent applications, and a guide to those intending to use a spectrometer or spectrograph for analysis and especially metallurgical analysis.

RECENT APPLICATIONS

1. " First of all, spectroscopy holds the premier position as a means of detecting and identifying minute quantities of the elements. A mere trace, perhaps half a milligram, of a soot-like stain on the lead of an electric lamp was carefully removed, transferred to the electrode of a small copper arc lamp, such as that already described, and, by the spectrum of its incandescent vapours, identified as a mixture of tungsten and iron. Not only was the presence of these elements demonstrated, but simultaneously the absence of most other elements in a proportion greater than one per cent. was signified. This last advantage of the spectrographic method, the demonstration of the absence of other elements, is often of more value than the evidence of traces of impurities." [1]

2. " A single drop of London tap water on drying down on an electrode and arcing reveals the presence of the sodium, magnesium and calcium it contains, although the total solids do not exceed the fiftieth part of a milligram or the three-thousandth part of a grain." [1]

3. " In the course of a spectrographic examination of the ashes of several drugs and of the ashes of the tinctures prepared from them (*Yr. Bk.* of *Pharmacy*, 1914, 361-370), it was discovered that boron was present in all." [1]

[1] Cantor Lectures, " Recent Applications of the Spectroscope and the Spectrophotometer to Science and Industry," by Samuel Judd Lewis, D.Sc., F.I.C., Ph.C., delivered before the Royal Society of Arts, April 11th, 18th, and 25th, 1921.

4. "Two glasses were examined and .... it was learnt that the first contained a notable quantity of zinc, which was not the case with the second." [1]

5. "The spectrographic method has been successfully applied to the determination of minute quantities of nickel in fats." [1]

6. Murphy and Lonsdale have found that, for brewery practice, it is not satisfactory to rely on a mere biological analysis of the air in the neighbourhood of foundries, smelting works, etc., and in both water and air analysis use the spectroscope as the only ready means of determining chemical constituents.[2]

7. Metals (*e.g.* zinc) have been detected in the animal organism by the spectrograph, as, for instance zinc in the ash of Cobra Venom by rays 4811, 4722 and 3345.[3]

8. The detection of traces of mercury in explosives can be most reliably effected by electrolysing a solution prepared from the explosive, using a platinum wire as electrode, and afterwards exposing the wire to a suitable electric discharge in a vacuum tube, and observing the spectrum by a visual spectroscope. As little as 0·000001 or even 0·0000001 gm. may be detected.

9. "The ease and value of the application of spectrum analysis to industrial chemistry appears to be appreciated in few of the large works laboratories of this country. For eight years this analysis has been of great value to the authors in both analytical and metallurgical work.

"To the analyst the complete qualitative analysis of an unknown alloy, revealed by a spectrogram, is a sure basis for the planning of the most direct and rapid method of attack. As the determination of each element proceeds, the purity of precipitates may be checked as often as desired. The spectrograph proves invaluable in the recognition of impurities, the separation of which would entail a lengthy and difficult procedure, or when the weight of an unknown is less than is necessary to complete the desired determinations. A few hundredths of a gram will usually suffice for spectrographic analysis.

"In the separation of the rarer elements, the spectrograph will show, with precision, the point where each step has been successful. In zinc of certain classes, indium, gallium, and germanium have been isolated

[1] See footnote on p. 2.

[2] "Emission Spectrography in Chemical Industry," Samuel Judd Lewis, D.Sc., F.I.C., Ph.C., *Journ. Soc. Chem. Ind.*, June 30th, 1916.

[3] A. de Gramont. *Compt. Rend.*, vol. 170, pp. 1037 to 1039.

in this way ; the presence of antimony in lake coppers has been proved ; and bismuth has been detected in zinc and in alloys where the presence of a few thousandths of one per cent. would be harmful. An antimony precipitate in a delicate determination may contain a considerable proportion of tin or arsenic, both of which will be revealed. The spectrograph is consequently important to the metallurgist as well as to the analyst.

" Impurities in raw material are often a source of annoyance, especially when their detection involves delay and costly analytical work. Whether low conductivity in copper is due to arsenic, nickel, or something else, may be quickly found out. Residual traces of boron, magnesium, manganese, silicon, vanadium, and other deoxidising agents are easily identified where wet analysis may fail to reveal their presence, even after days of effort. Complex alloys of any kind are dissociated by the spectrograph into a spectrum, the reading of which gives the elements present, together with an idea of the relative amounts of each. The secrets of the inventors of alloys and hardened metals are no great problems when, for their solution, one can depend on the application of the microscope and spectrograph." [1]

10. Iron and steel analysis and manufacture are subject to great help from spectroscopic investigation. The detection of traces of metals other than those usually assayed is frequently a matter of practical interest, while the spectrograph has also demonstrated the volatilisation of various metals such as zinc, bismuth, tin, copper, lead, etc., from molten iron. An easy and ready means of control is the comparison of the spectra of two specimens of similar steel for detecting their differences. If one steel be adopted as a standard, any number of steels may be compared with it as a matter of routine.

11. The inert gases argon, neon, etc., in the electric lamp industry, can be most readily and efficiently tested for their purity by simple spectroscopic observation.

12. The separation of sufficient of an impurity to determine its nature is often a lengthy process, sometimes almost impossible, but with a spectrometer the presence of certain lines characteristic of the impurity may be seen at once. To take one out of many such cases, how often will a careful worker have reason to doubt whether a separation by precipitation is complete—whether, for instance, the precipitate has been sufficiently washed ? In many cases the presence of so small a

[1] " Spectrum Analysis in an Industrial Laboratory," W. H. Bassett and C. H. Davis, *Trans. Amer. Inst. of Mining and Metallurgical Engineers*, read Feb. 1922.

proportion of the substance as one part in 100,000, sometimes very much less, can be seen at once and relied on without possibility of error.

WORKS OF REFERENCE

Among the most useful papers for reference as an index to particular applications are those by Pollok, Pollok and Leonard, and de Gramont, of which a list is given below. All these investigations were directed to establishing quantitative methods of spectrum analysis by means of the spectrograph, and they are therefore grouped together under that heading. But they include a thorough examination of the important " persistent lines " and " Raies Ultimes," and they are as valuable for qualitative as for quantitative work.

QUANTITATIVE SPECTRUM ANALYSIS

Hartley in 1882 first pointed out that " as the quantity of any element present in a substance is diminished, many lines due to that element cease to appear in the resulting spectrum." Those lines which are still present in the spectrum when the element is reduced to a very small quantity were called by Hartley the " persistent " lines. This work of Hartley (*Phil. Trans.* 1882 and 1884) was continued at Dublin by that of Pollok and others, and in France by the independent work of A. de Gramont.

De Gramont distinguished by the name of *Raies Ultimes* those lines in the spectrum of an element which are the last to disappear. These *Raies Ultimes* common to the Spark, Arc and Flame Spectra, include the rays which are spontaneously reversible.

The above workers have based on their researches methods of quantitative spectrum analysis of great technical importance.

Later investigations go to prove that the ultimate lines vary with the conditions of excitation of the source. De Gramont, 1914, finds, for instance, that they shift towards longer wavelength as the temperature diminishes : Pollok and Morrow, too, find that the ultimate lines with the vacuum tube are different from those with the spark. These observations, which were not altogether unexpected, do not however detract from the importance of the work on quantitative spectrum analysis. We therefore give here a bibliography of papers on the last named subject, with notes of the contents.

Author.	*Journal.*
Pollok.	Proc. Roy. Dublin Soc. (1907), **11**, 184-216. The persistent lines of Mg, Zn, Cd, Al, In, Th, Cu, Ag, Hg, Sn, Pb, Te, As, Sb, Bi, Be, Si (all as obtained by Hartley).
Pollok and Leonard.	Proc. Roy. Dublin Soc. (1907), **11**, 217-228. Quantitative spectra of Fe, Al, Cr, Si, Zn, Mg, Ni, Co.
Pollok and Leonard.	Ibid. (1907), **11**, 229-236. Quantitative spectra of Ba, Sr, Ca, Mg, K, Na.
Pollok and Leonard.	Ibid. (1908), **11**, 257-269. On the separation of cerium, lanthanum, and yttrium.
Leonard.	Ibid. (1908), **11**, 270-279. Quantitative spectra of Mo, W, Th, Zr.
Pollok.	Ibid. (1909), **11**, 331-337. Quantitative spectra of Ti, U, V. Ibid. (1909), 338. The spectrographic analysis of a specimen of commercial thallium.
De Gramont.	Compt. Rend. (1907), **144**, p. 1101-1104. The *raies ultimes* of calcium, strontium, copper, silver, magnesium, zinc, aluminium, thallium, germanium, tin, lead, bismuth, chromium, and iron.
De Gramont.	Compt. Rend. (1908), **146**, 1260-1263. The *raies ultimes* of the metalloids, tellurium, phosphorus, arsenic, antimony, carbon, silicon, and boron.
De Gramont.	Compt. Rend. (3 Jan. 1910), **150**, 37. The distribution of certain persistent lines in the solar spectrum. An examination is made for the lines of K, Rb, Mg, Ca, Sr, Ba, Sc, Al, Ti, Pb, V, Cr, Mn, Fe, Ni, Co.
De Gramont.	Compt. Rend. (January 1910), **150**, 154. A similar examination of the distribution in stellar spectra.
De Gramont.	Compt. Rend. (25 July, 1910), **151**, 308-311. The place of the *raies ultimes* with regard to the spectral series, in particular the 2138 line of Zn. 2365 line of Cd. 2536 line of Hg.

Author.	*Journal.*

DE GRAMONT. Compt. Rend. (July, 1912), **155**, 276-279.

A further development in the technique, particulars of a new Hilger spectrograph, describes how certain causes of instrumental errors were overcome, and gives details of the *raies ultimes* for chromium, manganese, iron, nickel, and cobalt.

DE GRAMONT. Compt. Rend. (1918), **166**, 94.

Researches on the line spectrum of titanium. An illustrated description of his sparking apparatus is given. The chief lines of titanium are grouped after the manner employed by Hartley and Pollok, and the application of the method to metallurgy is described.

DE GRAMONT. Compt. Rend. (1918), **166**, 365.

The *raies ultimes* of colombium (niobium) and zirconium are investigated. Reference is made to a similar investigation by M. A. P. de Sampio Forjaz (Arquivos da Univ. de Lisbonia, vol. iii. 1916) on the lines of zirconium and uranium.

DE GRAMONT. Compt. Rend. (1918), **166**, 477.

The persistent lines of boron : it is shown that the appearance of wavelength 3451·2 shows that the substance is present at a concentration of 1/10,000 or over ; wavelength 2497·8 for a concentration of 1 part in 100,000 ; and wavelength 2496·8 for 5 parts in 100,000.

" L'intensité notable de ces trois raies du bore à 67 dix millièmes dans le spectre d'étincelle de cet acier permet donc de les indiquer comme susceptibles d'une utilisation pratique certaine pour les analyses métallurgiques."

DE GRAMONT. Compt. Rend. (1920), **171**, 1106-1109.

Sensitive Spectral Lines ; Ultimate Lines in the Spectra of 83 elements. The arrangements employed in the work here described were the same as used for determining the ultimate lines in the spectrum of titanium. The present paper gives the ultimate lines in the dissociation spectra of 83 elements. The results are presented in tabular form. One column gives the ultimate lines observed visually, a second column the

Author.	*Journal.*
	ultimate lines obtained when using a "crown uviol" spectrograph, including lines from λ4800 down to λ3170, and a third column gives lines below λ3170 obtained with a quartz spectrograph.
De Gramont.	Revue de Métallurgie, 19 année, No. 2, Février 1922, "Sur l'emploi de l'analyse spectrographique en métallurgie." A description of the properties of the sensitive rays and their application in quantitative metallurgical analyses, including analyses of modern steels.

A summary of the results of Hartley, Pollok, Leonard, and A. de Gramont, with the wavelengths of all the persistent lines referred to, will be found in *Wavelength Tables for Spectrum Analysis*.[1]

Another and quite different method has been developed by Hill and Luckey (*Trans. American Electrochemical Soc.* (1917), **32**, 335), depending on a difference in volatility in the constituents of an alloy. They use the arc discharge, and measure the time required for a line to disappear when a given weight of the unknown mixture is burned in the crater of the arc. This method is obviously limited in its application, but in the instance of lead in copper, a range of .004 – .216 per cent. can be estimated with all the precision required in refinery work.

At a discussion of the above paper, M. G. Lloyd of the Bureau of Standards, Washington, stated that a spectrographic method of quantitative analysis was in use at the Bureau for determining the impurities in tin boiler plugs, and that when the impurity does not amount to more than 0.1 per cent. the results are quite as reliable as those obtained by analysis. He adds: "Quantitative spectroscopic analyses of steel have been made, especially for the determination of chromium and titanium. For such elements as niobium and molybdenum the spectroscopic estimation of small quantities is more reliable than chemical analysis." [2]

Mottram also adopted the principle of correlating quantity with the time required for given spectrum lines to disappear, in determining the alkali metals in animal tissues and blood, 0·0000002 gm. of potassium in 0·02 c.c. of solution being a working quantity.

[1] See p. 73.

[2] Further applications of quantitative spectrum analysis as practised at the Bureau of Standards are given in Scientific Paper No. 444 of the Bureau of Standards (July 1922). The examples given relate to the quantitative estimation of impurities in tin, gold and platinum.

The spark is usually adopted in quantitative work, but S. Judd Lewis has recently advocated the arc for general laboratory work, and shown that results which are both reliable and fairly approximate may be obtained with ordinary care, thus bringing the work within the scope of the ordinary laboratory. (See Cantor Lectures, 1921, April 11th, 18th, and 25th, published by the Royal Society of Arts.)

FURTHER WORKS OF REFERENCE

The chemist provided with the Hilger instruments referred to below, with the instructions for use which accompany those instruments, and with the *Wavelength Tables for Spectrum Analysis*, published by Adam Hilger, Ltd.,[1] will require nothing further for the successful employment in his daily work of spectrographic analysis. For those who are interested in spectroscopy for its own sake a few words on the literature of the subject may be acceptable.

With regard to qualitative spectrum analysis, which has developed from Kirchoff and Bunsen's early work, the literature is very extensive.

For methods of obtaining spectra with arc or spark discharges, the following text-books may be consulted.

BALY.	*Spectroscopy.* Longmans, Green. London.
WATTS.	*Index of Spectra* (1889 to 1921). Longmans, Green. London. A number of appendices have been published, full particulars of which can be obtained from Adam Hilger, Ltd.
HAGENBACH AND KONEN.	*Atlas of Emission Spectra of most of the elements.* Translated by KING. Wesley, London.
URBAIN.	*Spectrochimie.* A. Hermann & Fils, Paris.

The spectroscopic notes on p. 55 *et seq.* of Hagenbach and Konen give much information regarding the setting up of apparatus, exposure, etc. Urbain's book includes instruction for analysis of the rare earths, and for general spectrum analysis.

Lines in the Arc Spectra of Elements (F. Stanley)[2] is a list of the principal lines in the arc spectra of most of the elements arranged in order of wavelength. A much appreciated feature of this book is that opposite each

[1] See p. 73. [2] See p. 73.

line of an element the next prominent line of that element is given. The book is very useful in a rapid preliminary analysis.

Not all the rarer elements are included in the above atlases ; more complete works are :

Eder and Valenta.	*Atlas Typischer Spektren* (Wien, 1911).
F. Exner and E. Haschek.	*Wellenlängen Tabellen für Spektral-analytische Untersuchungen auf Grund der Ultra-Violetten Funkenspektren der Elemente.* (Leipzig and Wien, 1902.)
F. Exner and E. Haschek.	*Wellenlängen Tabellen . . . Bogenspektren* (1904).
F. Exner and E. Haschek.	*Die Spektren der Elemente bei Normalen Druck.* I. Hauptlinien der Elemente und Codex der Starken Linien im Bogen und Funken ; II. Die Bogenspektren. (Leipzig and Wien, 1911.)
Kayser.	*Spektroskopie*, vols. v. and vi.

Kayser's great book on " Spectroscopy " is, of course, a mine of information on every branch of spectroscopy. It is divided into the following sections :

Volume 1. History of Spectroscopy and Spectroscopic Apparatus.
Volume 2. Emission and Absorption, including the Zeeman effect.
Volume 3. Absorption and Absorption Spectra.
Volume 4. Dispersion, Phosphorescence, and Fluorescence.
Volume 5. Spectrum Analysis and Wavelength Tables, etc.
Volume 6. Wavelength Spectra of Metals, etc.
Volume 7. Part I. Wavelength Spectra of Metals, etc.

Volume 7 is expected to extend to three parts. It is intended to include all work done in 1923, and will comprise measurements made since 1908.

Many valuable series of measurements have been published in the *Astrophysical Journal* and in the *Zeitschrift für Wissenschaftliche Photographie.* The *International Tables of Constants* also include collections of spectroscopic measurements. Tables for the Schumann region are given in Lyman's *The Spectroscopy of the Extreme Ultra-Violet.* (Longmans, 1914.)

APPARATUS

The letters and numbers in the text are those of the Publishers' catalogue of Scientific Instruments.

Means of Excitation of the Emission Spectrum.

There are three main ways of causing the sample under test to exhibit a spectrum for spectroscopic analysis : by the flame, by the arc, and by the spark.

1. *Flame Spectra.* Every chemist is familiar with the production of flame spectra. Their use is limited in practice to the identification of the alkali metals, of indium and of thallium. The methods of Kirchoff and Bunsen for their production have not been fundamentally altered, but certain improvements in technique have been introduced, of which we may cite those of Gooch and Phinney.[1] (For spectrum burner, see Catalogue, No. F. 289.)

2. *Arc Spectra. The Arc with Carbon Poles.* Purified electric carbons (sold by us for this work) are used in a simple form of arc lamp. The positive carbon is cored, and a small cup scooped out to contain a minute quantity of the sample under examination. The lamp is connected to the electric mains through a suitable resistance, and when the arc is struck the light emitted gives the spectrum of the whole metallic contents of the sample. This method is suitable when the sample is in the form of grains or powder. (See Catalogue, Nos. F. 4, F. 284, F. 129.)

3. *Arc Spectra. The Arc with Copper Poles.* The arrangement is similar to the above, but instead of scooping out a cup in the lower pole it suffices to place a few milligrams of the substance on the lower copper pole. Poles of high grade electrolytic copper are supplied by us for this purpose. (See Catalogue, No. F. 127.)

4. *Arc Spectra. The Arc direct from the Sample.* If the samples are in metallic form, two pieces can often be conveniently used to form the poles of the arc.

5. *Spark Spectra. For Solids.* If the samples are, although in metallic form, too small for an arc to be run with them as poles, they can be used as sparking electrodes. (See Catalogue, Nos. F. 281, F. 282, F. 283, F. 284, F. 285, F. 3.)

[1] *Am. Journ. Sci.*, 3rd Ser., Vol. 44, p. 392. "The Quantitative Determination of Rubidium by the Spectroscope."

6. *Spark Spectra of non-conducting powders.* An important modification is by the method of " sels fondus " (A. de Gramont). In this method non-conducting powders such as those of slags, stony minerals, glasses, precipitates, mixed and finely ground with four or five times their weight of sodium or lithium carbonate, are then put in a platinum cup 20 mm. diameter and 5 mm. deep. The mass is fused by a Meker burner, and the spark passed between the fused mass and an electrode of platinum.

7. *Spark Spectra. For Liquids.* If the circumstances of the case make it convenient or desirable to have the substance in the form of a solution, the " Pollok sparking tube " is convenient. With this device the spectrum of the substance can be obtained from a small quantity of solution containing it. (See Catalogue, No. F. 66.)

Full particulars of all the above arrangements will be found on reference to the catalogue under the sections and numbers given at the end of each paragraph.

Spectrometers.

For visual spectrum analysis one of the modern " Wavelength " forms (introduced by Adam Hilger, Ltd., in 1904) is essential.

The standard model and that generally to be recommended is the Hilger Wavelength Spectrometer, D. 1. A larger and more accurate, D. 19, and a smaller student's form, D. 45, are also made; both of the same type as the D. 1.

A readily portable instrument which takes up very little room, either in use or when put away in its case, is provided by the Hilger Chemical Spectrometer, D. 39.

For flame spectra the simple " Flame " Photoscale Wavelength Spectrometer, D. 48 or D. 49, is better than any of the above.

Spectrograph.

Useful as are the above visual spectrometers, most of the work in an industrial laboratory calls for a spectrograph (viz.—an apparatus for photographing the spectrum), and moreover for a quartz spectrograph. The chemist can often, by a glance in a visual spectrometer such as those named, assure himself of the presence or absence of a particular metal, but there are three important reasons rendering the quartz spectrograph more generally useful where it is not possible to have both. (*a*) Many

of the most distinctive and sensitive spectral lines lie in the ultra-violet part of the spectrum, which is invisible to the eye. (*b*) A permanent record is often required. (*c*) The routine of taking a spectrogram from any sample can be readily and reliably carried out by any intelligent laboratory assistant, and the chemist can then carry out the examination of the photograph at his leisure.

As spectrograph a Hilger Quartz Spectrograph, E. 34, is that to be recommended for general work. This instrument has a wavelength scale which is photographed on the same plate as the spectrum, and is of great help in recognising and indicating the location of lines or of distinctive groups of lines. A reproduction of spectrograms taken on this instrument forms the frontispiece of this book.

For laboratories where alloys are frequently to be examined which contain large proportions of Iron, Nickel, Tungsten, Titanium, and other metals which, like these, have highly complex spectra, the more powerful Hilger Quartz Spectrograph, E. 1, or its cheaper form E. 30, is to be preferred. The Uviol Glass Spectrograph E. 42 has also been strongly recommended for general metallurgical analysis including that of steels.

Full particulars of these Spectrographs and their accessories will be found in Sections E. and F. of our catalogue. A number of diffraction grating spectrographs will also be found described there, but we do not usually recommend these for such work as is dealt with in this book.

METHODS OF USE

Such spectrographic outfits as those described above permit the discovery and identification of traces of all the metals as well as of the four non-metals boron, silicon, phosphorus and arsenic.

The general methods of setting up and using the Hilger Spectrographs are completely described in the instructions issued with each instrument ; while for the methods applicable to special classes of work the carefully selected papers mentioned above may with great advantage be referred to.

We may here confine ourselves to pointing out that the questions the chemist may refer to the spectrograph are broadly divisible into two classes.

(i) Does a given substance contain this, that, or the other metal ?
(ii) What are all the metals present in a given substance ?

The most direct and simple way of dealing with the first class of question is to take side by side comparison spectra of the substance (*a*) under examination, and of the pure substance (*b*) whose presence or absence is of interest. The presence in the spectrogram of (*a*) of lines due to (*b*) conclusively demonstrates the presence of (*b*) in (*a*).

If a complete list of all the metals present is required, it is sometimes quicker to take comparison spectra (*a*) of the substance under examination and (*b*) of the combined spectra of all the metals (if any) known to be present. The wavelengths of the lines present in spectrum (*a*) and absent in spectrum (*b*) are then carefully measured with the aid of a photomeasuring micrometer, L. 1 or L. 2, and such measurements enable the substances giving these unknown lines to be stated without doubt.

An excellent account of this latter method of work is given in the paper by Bassett and Davis mentioned on p. 4 (footnote).[1]

Where it is adopted it is necessary to have a list of accurate standard wavelengths for reference, and to meet this need the publishers of this book have prepared the two following publications :—

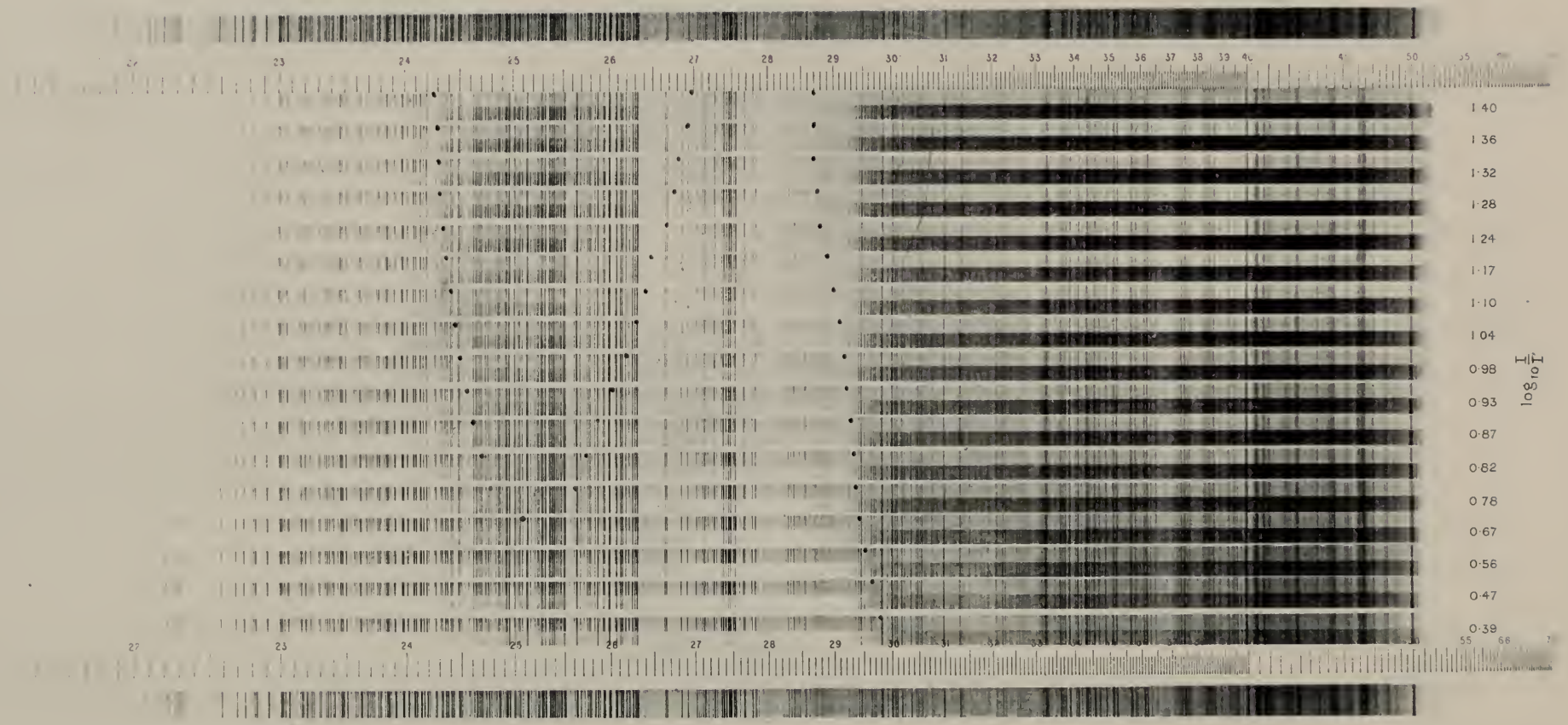
1. Photographic reproductions of the Iron Arc Spectrum, marked with wavelengths.[2]

2. A resumé of the whole of the wavelengths adopted up to the present date by the International Solar and the International Astronomical Unions ; together with tables of the distinctive lines of most of the metallic elements (*Wavelength Tables for Spectrum Analysis*).[3]

There is one other method which will be found naturally to suggest itself with experience. In every spectrum there are one or more groups of lines which are highly characteristic of the metal, and these become familiar and recognisable at a glance to those making frequent use of the spectrograph.

A condensed account of the technique of Spectrum Analysis is contained in " Spectrum Analysis with Hilger Instruments " 4.

[1] Reprints can be obtained from Adam Hilger, Ltd., see p. 73.
[2] See p. 73.
[3] See p. 73.
[4] See p. 73.



ABSORPTION SPECTRUM (PART ONLY) OF PSEUDO-GLOBULIN 0·092 PER CENT SOLUTION BY THE SECTOR SPECTRO-PHOTOMETRIC METHOD.

SECTION II

ABSORPTION SPECTRA AND SPECTROPHOTOMETRY

Applications of Qualitative Absorption Spectra.

The investigation of ultra-violet absorption spectra has thrown a good deal of light on the constitution of organic substances. The work of Hartley, Dobbie, Baly, Stewart, Kayser and others demonstrates the importance of this side of the subject. The utility of observations in the ultra-violet has been repeatedly confirmed, especially in the case of substances such as isatin which may exist in tautomeric forms. In such cases, the spectrograph is one of the readiest means of deciding between alternative formulae for the structure of a compound. (See *Journal of the Chemical Society* (1900), **77**, 839, and Kayser's *Handbuch*, especially vol. iii.) A number of similar cases are referred to in the British Association Reports for 1901 and following years.

An interesting study in connection with the constitution of organic substances is that of the ultra-violet absorption spectra of alkaloids. Many communications on this subject appear in the pages of the *Journal of the Chemical Society*, by Hartley and by Dobbie and his co-workers. One of the features which renders this method of investigation so valuable is the fact that only very small quantities of the pure substances are required, and the manipulation is easy. Frequently one or two centigrams suffice (see Ley, *Farbe und Konstitution bei Organische Verbindungen*, Leipzig) for determining the absorption curve of the alkaloid by the characteristics of which the individual alkaloid may usually be identified. Dobbie has shown that the absorption bands so obtained are in fact the bands due to the ringed nucleus of the molecule of the alkaloid. Thus the bands of quinine, cocaine, and morphine are practically identical in position with those of 6-methoxyquinoline-benzoic acid, and catechol respectively. Emetine, cephaeline, corydaline, laudanosine and certain other alkaloids all give absorption spectra showing that they contain the catechol grouping. So delicate is the method that such a minute quantity

of pyridine as 0·00001 gram in 100 c.c. of aqueous ammonia can be readily detected by the effect on the ultra-violet spectrum. (See Hartley and Dobbie, *Journ. of the Chem. Soc.* (1900), **77**, 318.)

As little as 3 mg. of cocaine in 100 c.c. can be identified by its characteristic band in the ultra-violet. It is interesting to note that this band is similar to that due to benzoic acid,[1] which fact furnishes additional evidence of the presence of a benzoic acid residue in the molecule of cocaine.

Very minute quantities of benzoic acid itself can also be identified by this method, a matter of some importance having regard to the difficulty of detecting this acid. Again, as little as one milligram of phenol in 100 c.c. is shown by its absorption spectrum.

Upon similar lines Dr. Maurice de Laet of Brussels has applied the absorption spectra of the alkaloids to the purposes of toxicology. Using a Hilger quartz spectrograph and an adjustable observation cell similar in principle to the Baly tube, he obtained twenty to twenty-five good spectrograms "45 mm. long and 2 mm. high" on a plate, sufficient for directly plotting the curve, with wavelengths for abscissae and thickness of the layer of solution for ordinates. The alkaloid in the material under investigation is extracted by one of the usual methods, and the acid solution containing 0·1 to 1 mg. of the alkaloid in a c.c. is examined spectrographically. The identity of the alkaloid may then be established by the form and dimensions of the absorption curve, while a fair approximation to the concentration is determinable. (*L'indentification medico-legale des alcaloïdes par la spectrographie*, par le Dr. Maurice de Laet, Bruxelles, 1921.)

By photographing the ultra-violet absorption spectra of the vapours, extremely minute quantities of organic substances such as benzene, and also certain inorganic substances, can generally be identified by the large number of sharp narrow bands which occur in their absorption spectra.

Absorption spectra of gases have frequently been studied with results of the highest interest to science. A notable example of a quantitative method as applied to industry is due to Robertson and Napper (*J. Chem. Soc.*, 1907, T. **91**, 761, 786), who, using a Hilger No. 1 table spectroscope fitted with a camera, worked out a simple means of determining a few hundredths of one per cent. of nitrogen peroxide (NO_2) in mixtures of gases resulting from the decomposition of gun cotton and the like.

[1] That is as far as an ordinary comparison of their spectra has revealed. No truly quantitative measurements (as by means of the Sector-photometer) have apparently been made at present.

The method has been found trustworthy and has been practised in Government laboratories.

For practical work in the above fields a small quartz spectrograph, such as the Hilger E 31, is sometimes even better than a larger, such as the E 3, since the wide bands in the neighbourhood of 200 $\mu\mu$ are sharper in the small instrument.

By far the greater part of the above work has been carried out without quantitative measurements of the absorption at each point of the spectrum. It does not seem even yet generally realised that apparatus is available whereby such work can be carried out, even in the ultra-violet region.

Encouraging as has been the success attending the study of alkaloids and similar substances in relation both to pure science and to toxicology, by the older methods, a still higher degree of precision is attainable with the new sector spectrophotometers presently to be described : moreover, with them considerably smaller quantities of the substance suffice, and the work is truly quantitative.

Spectrophotometry as Applied to Absorption.

Spectrophotometry has made great progress in recent years, and there can be little doubt that as its value is appreciated it will become the only method by which absorption spectra are studied, except when no more than qualitative results are required. It has for its object the precise measurements of the absorption at every wavelength in that region of the spectrum concerned. Although at first sight this may appear to be outside the range of ordinary practice, it is found that the object is readily attained by means of a good spectrophotometer.

These instruments fall into two main classes, the one determining its measurements by interposing a shadow of known dimensions, *e.g.* the sector spectrophotometers, for study of both the ultra-violet and visible regions ; the other, usually graduated by means of some polarising arrangement, for investigating the visible region.

In either case they enable the Bunsen-Roscoe " extinction coefficient " to be *measured* for any substance, for any wavelength.[1]

[1] The extinction coefficient is the quantity a in the relation :

$$\frac{I}{I_1} = 10^{ad},$$

where I is the light entering the medium, I_1 that transmitted (before reflection occurs at the leaving surface), and d the thickness in cms. of the medium traversed by the light (Bunsen and Roscoe, *Pogg. Ann. der Pysik and Chemie*, Bd. CI (Bd. 177 of the entire series), p. 238.

Sector spectrophotometers for exploring the ultra-violet region are a new invention.

Professor Kayser, writing in 1908, drew attention to the unsatisfactory nature of the work which had been and was then being done in absorption spectroscopy owing to its being merely qualitative,[1] and it was the remark of that authority which induced Adam Hilger Ltd. to originate the first ultra-violet spectrophotometer which was put on the market. It must not be forgotten that not only the intensity, but the actual position of the maximum of an absorption band is undetermined until quantitative measurements have been made, since any variations throughout the spectrum, whether of intensity of the light source, of sensitiveness of the photographic plate, or of dispersion, may cause the maximum of absorption to appear to be in a position different from that of the actual maximum. All absorption work, therefore, which is done other than quantitatively is subject to this criticism.

But exact knowledge of the position and intensity of the maxima of absorption are not the only advantage to be gained by using a photometer ; the form of the whole absorption curve is readily defined with the utmost precision, in contrast to the difficult and often ill-defined delimitation of the bands by the older method. The advantage of the spectrophotometric method is readily realised by considering problems which would be quite or practically insoluble by older methods, that is, in cases where the question involves the precise measurement of quantities.

" The Quantitative Absorption of Light by Simple Inorganic Substances " has been studied by Branningan and Macbeth (*J. Chem. Soc.*, T. 1916, **109**, 1277-1286). They have shown that the halides of the alkali metals exhibit well-defined absorption bands, the dimensions of which are an expression of the atomic weights of the constituent elements. This is a direct result of using a photometer, for only shortly before an examination of some of these same salts by the older method (*J. Chem. Soc.*, 1912, T. **101**, 266), led to the conclusion that they were entirely diactinic.

[1] *Handbuch der Spectroscopie von H. Kayser*, Band 3, S. : 49 " Aber alle diese Methoden eignen sich doch nicht zu einer genauen Bestimmung der Absorptionsconstanten für viele Substanzen und verschiedene Wellenlängen. Trotz der zahlreichen im Vorhergehenden besprochenen Apparate, musste man bis vor Kurzem sagen, dass es kein brauchbares Instrument für Photometrie im Ultraviolett giebt mit dem man etwa daran hätte denken können, eine ausgedehnte Untersuchung z. B. organischer Substanzen vorzunehmen. Man war ausschliesslich auf die später zu besprechende Methode angewiesen, die namentlich von Hartley ausgebildet und durchgeführt ist, die aber keine Messung der Constanten, höchstens eine Schätzung über die Grösse der Absorption zulässt."

Changes in molecular complexity of solutions of cupric chloride when alone and when associated with other salts have been investigated by reference to spectrophotometric data (G. H. Getman, *J. Physical Chem.*, 1922, **26**, 216-246).

Spectrophotometric identification of phenols claimed the attention of H. Gsell (*Zeit. anal. Chem.*, **55**, 1916, 417). The phenol is converted into the alkali salt of its phthalein, and identified by the position of the absorption band.

A study of the extinction coefficients of the three chief proteins of blood serum, namely, albumin, pseudo-globulin, and eu-globulin by S. Judd Lewis (*Proc. Roy. Soc.*, B, 1922, 189), led to the hypothesis that each of these proteins is composed of two or more proteid substances in physical association.

Work seeming to promise results of considerable interest has been conducted on the examination of the ultra-violet absorption of blood serum by S. Judd Lewis,[1] and recently by Tadokoro[2] and Nakayama.[3] The former observer claims to have found in this way the existence of specific changes in the blood serum in the early stages of certain diseases, and the latter have observed changes in the blood serum under various conditions of physiological interest.

Charles Dhéré has investigated the ultra-violet absorption spectra of several substances of physiological interest, of which the following may be mentioned: sarcine (6-oxypurine), xanthine (2·6-dioxypurine), uric acid (2·6·8-trioxypurine), which under equal conditions absorb light as far as wavelengths 2748, 2872 and 3060 A. respectively, signifying that they form a series (*Compt. Rend.* 1905, **141**, 719). The spectroscopic properties of vegetable pigments have been investigated. Chlorophyll has been shown to exhibit several bands, and, in the pure state, to be remarkably transparent in the extreme ultra-violet (*Compt. Rend.* 1912, **155**, 653).[4] Carotin and xanthophyll have been similarly studied (*Compt. Rend.* 1913, **157**, 501).

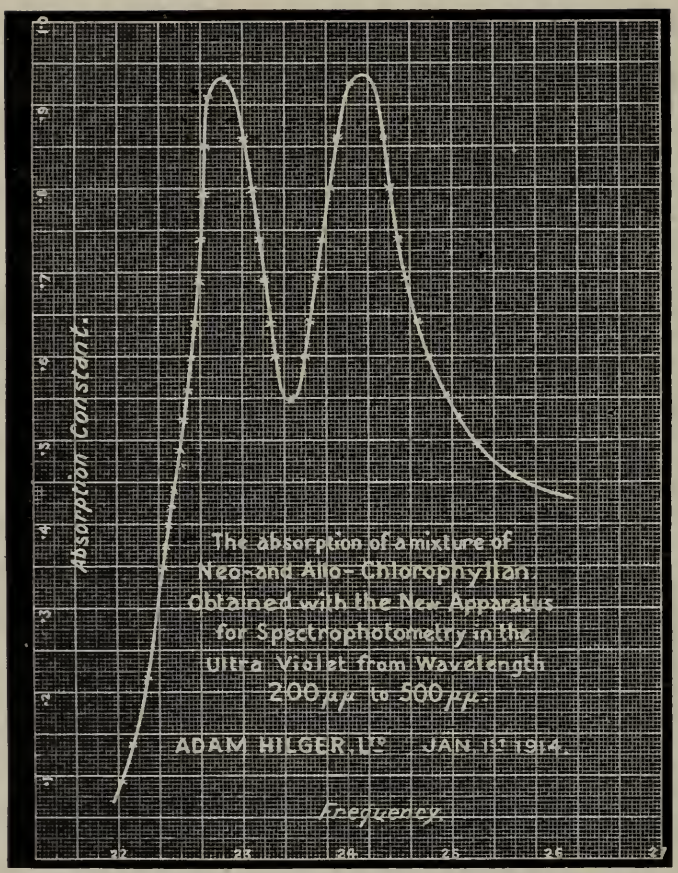
The foregoing data relate to blood serum and vegetable pigments.

[1] S. Judd Lewis, "The Ultra-violet Absorption Spectra of Blood Sera" (*Proc. Roy. Soc.*, B, **89**, 1916, 327).

[2] "Ultraspectroscopic Studies on Blood Serum," by T. Tadokoro. From *Journ. of Infectious Diseases* (January 1920), **26**, No. 1, 1-7.

[3] "Ultraspectroscopic Studies on Blood Serum," by T. Tadokoro and Y. Nakayama From *Journ. of Infectious Diseases* (January 1920), **26**, No. 1, 8-15.

[4] See also the curve on p. 8.



The Chlorophylls and their derivatives have been widely studied spectroscopically. Reference may be made to a lengthy paper by Jacobson and Marchlewski (*Biochem. Zeit.*, **40**, 1912, 296-306) where it is shown that the best method of determining the proportions of allo-Chlorophyllan and neo-Chlorophyllan existing in naturally occurring mixtures is quantitative absorption spectroscopy. The accompanying graph, determined by means of a Hilger sector spectrophotometer,[1] expresses by the magnitude of the band in the region of shorter wave-length (or of greater frequency) the concentration of neo-Chlorophyllan, and by that of the other, the proportion of allo-Chlorophyllan.

The spectroscopy of the colouring matters of blood, haemoglobin, oxyhaemoglobin and carboxyhaemoglobin is well known, but an interesting fact not so generally known is the discovery made by Hoppe-Seyler in 1879, that the absorption spectrum of haemotoporphyrin derived from the haemoglobin of blood is very similar to that of phylloporphyrin obtained from chlorophyll. Subsequent work has shown that

[1] See p. 74.

the colour-bearing groups of these two substances are practically the same, indicating a very important connection between plant and animal physiology.

Even in the visible region Spectrophotometry has not received in the chemical laboratory the attention it deserves. Yet it is necessary to remember only one or two classical instances of its application in order to remind oneself of the very great importance of this physical measurement. Such investigations as the determination of CO in blood by Vogel and the separation of Neodymium and Praseodymium by Auer v. Welsbach may be cited in this connection.

An important industrial application of the spectrophotometer is the testing of optical glass, goggle glasses, etc., for visual, ultra-violet or infra red absorption.

Spectrophotometry in the Visible Region.

Applications of visual spectrophotometry are naturally limited to those substances which exhibit absorption in the visible region.

Dyes, of course, are in this category, and among the most important industrial applications of the visual spectrophotometer are the identification, estimation and analysis of dyes. This application is so far confined among dye manufacturers and users to a very limited number; but it is claimed by one of the latter that the saving to his firm in cost of dyes alone effected by the use of the spectrophotometer during 1914 to 1919 is to be reckoned in tens of thousands of pounds.[1]

Fig. 4 illustrates how a dye analysis would be conducted by means of the Hilger Wavelength Spectrometer with Nutting Photometer (D. 1 and H. 56), this combination forming a convenient and efficient spectrophotometer. A solution of known strength is prepared from a reliable sample of the dye under consideration, the solution being of such strength as to give

[1] Quantitative measurements of absorptions of seven permitted food dyes are given for the infra-red, visible, and ultra-violet regions in Scientific Paper No. 440 (June 1922) of the Bureau of Standards. (Naphthol Yellow S, Ponceau 3R, Orange I, Amaranth, Indigo Disulpho Acid, Erythrosine, Light Green S. F. Yellowish.)

Papers by Walter C. Holmes, of the Colour Laboratory, Bureau of Chemistry, Washington, deal with acid dyes of the patent blue type (*Ind. and Eng. Chemistry*, Aug. 1923), and with basic fuchsins (*ibid*, Jan. 1925).

In these papers the general principles of identification are presented. The writer believes they will prove susceptible of extensive application, and curves and tables are given in which various significant characteristics of the individual dyes are recorded in definite spectrophotometric terms.

A Hilger-Nutting Spectrophotometer, made by Adam Hilger Ltd., was employed in the above experiments.

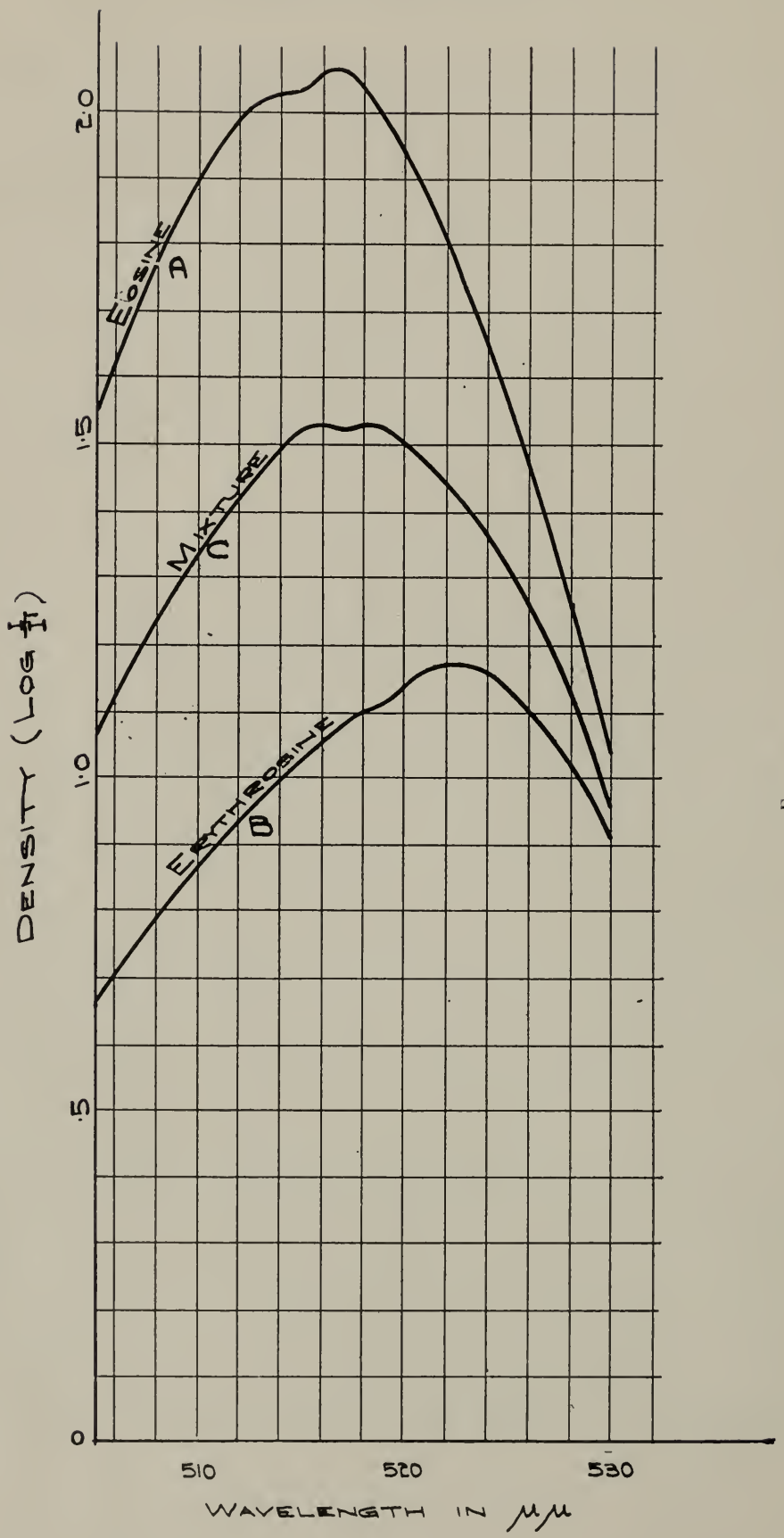

DENSITY (LOG $\frac{I_0}{I}$)
2.0
1.5
1.0
.5
0
EOSINE
A
MIXTURE
C
ERYTHROSINE
B
510
520
530
WAVELENGTH IN μμ

FIG. 2.

an accurately measurable absorption in the region of maximum absorption. Such a solution will require to be only a very dilute one. This solution is then spectrophotometered—namely, its extinction coefficient is measured for a series of wavelengths by means of the Nutting Photometer used in conjunction with the Hilger Wavelength Spectrometer. The results are plotted, and the curve kept as a permanent reference. When testing a sample of what purports to be the same dye at any future time, a solution of equal strength by weight is made up and similarly spectrophotometered. The densities are then plotted on the same sheet as the standard curve, and any non-coincidence of the two curves indicates a corresponding difference either in strength or nature of the dye. If the difference is in the strength only (through dilution by a colourless substance, *e.g.* dextrine), all the ordinates are reduced in like proportion. A particular case is illustrated in Fig. 2, showing curves of solutions of eosine and erythrosine, and a mixture of the two.

It will readily be understood that the instrument can be used to measure the proportions in which two dyes are mixed. For instance, in the curves shown, let us suppose A and B to be our standard curves of known strengths of reliable eosine and erythrosine, C is a mixture of the two, whose proportions are unknown, as also whether it is merely A and B mixed, or whether a diluent has been added.

Let m be the proportion of A in the mixture before dilution, and let the mixture be diluted by some inactive substance so that its weight before dilution is to its weight when diluted in the proportion of 1 to n. Then, in Fig. 4, if a, b, and c represent the ordinates of any wavelength of curves A, B, and C respectively

$$m(a-b)+b=cn.$$

Spectrophotometry in the visible region also has been applied to the study of the progress of reactions. An interesting example is the determination of the rate of formation of diazo-compounds, by E. Tassilly (*Compt. Rend.* **157**, 1913, 1148; **158**, 1914, 335, 489). Portions of the reacting mixture are removed at frequent intervals, and the intensity of the transmitted light in the region of greatest absorption is rapidly determined by means of the spectrophotometer. The several curves indicate great differences in the rate of reaction of the various amines.

The spectrophotometer has been employed by J. Boyer (*La Nature*, 1922, 372), in the evaluation of dyes for industrial purposes, showing, for example, that two *noirs diamants* found to be similar colorimetrically,

but capable of imparting different shades to wool, give different absorption spectra capable of explaining the divergence in their technological applications. The assay of the colouring powers of dyes is also described.

The spectrophotometer has also found several applications in the chemical laboratory at the hands of Ch. Féry and E. Tassilly ("La Spectrophotometrie en Analyse," *Annales des Falsifications*, Fevrier 1913), *e.g.* the ferric salt in a natural water is converted into sulphocyanate and the proportion determined by the intensity of the absorption of the solution at suitable wavelengths. The advantage over colorimetry lies in the fact that tints due to disturbing elements are without effect. The results are usually within 1 per cent. of the truth, thus $0{\cdot}0075 \pm 0{\cdot}000075$. Similarly, the traces of copper extracted from foods may be determined to 0·0002 g. per c.c.; thus 0·0019 g. copper was found where 0·002 g. had been used.

Another suggestion is culled from the *Annual Reports of the Chemical Society*, 1916, p. 167. This describes a method for getting a visual spectrophotometric effect by comparing the intensity of the absorption at any wavelength with that of a solution of equimolecular quantities of potassium chromate and copper sulphate in 2 N-ammonia solution.

Finally may be mentioned the use of a specialised visual spectrophotometer in the photographic plate industry. The well known and widely used set of apparatus originally made by Adam Hilger Ltd. for Dr. C. E. Kenneth Mees will be found fully described by him in the Photographic Journal for July, 1904. (Catalogue items H. 1, H. 7, H. 9, etc.)

Apparatus and methods for absorption spectra in the ultra-violet up to wavelength 2100 A. are described below under that heading.

The *infra-red* and the *extreme ultra-violet* regions are not less important from the standpoint of pure science than the visible and the ultra-violet as far as a wavelength of 2100 A., but the circumstance that apparatus of special and less familiar construction is necessary for their study has restricted the scope of operations. Apparatus for these regions convenient to manipulate has been available for some time (D. 35 and E. 50), and the exploration of both these outlying regions should lure both the student of pure science and the technological inquirer. Baly has shown that, considering the spectrum from the far infra-red to the extreme ultra-violet, very simple relations between the wavelengths of the bands in these several regions are discoverable, relations which were quite unrecognisable in a study confined to the ordinary compass (see *Nature*, 1921, p. 311). The most obvious technological application of infra-red spectroscopy is

the determination of the selective diathermancy of various transparent and opaque screens.

Apparatus and Methods for Absorption Spectra in the Ultra-violet up to Wavelength 2100 A.

Measurements of absorption acquire their chief interest when plotted on a wavelength scale (a frequency scale would be preferable on theoretical grounds). With all the instruments referred to below the necessary readings for doing this are immediately at hand without the necessity of the purchaser carrying out laborious calibration himself.

An apparatus for *measuring* the absorption enhances enormously the importance of absorption spectra, for not only does it enable the true form of the absorption curves to be studied, but it makes possible quantitative measurements of the absorbing substance.

In the visible region all that is required is a Hilger Wavelength Spectrometer (such as the D. 1) fitted with shutter eyepiece (F. 40), and a Hilger-Nutting photometer (H. 56).

For the ultra-violet, a combination of a quartz spectrograph with a sector photometer (E. 3 and H. 16) is required, together with a suitable light source; and these will now be described.

With such a combination the whole of the data for an absorption curve can be obtained on a single photographic plate, and such a curve uniquely characterises and defines the amount of the substance examined.

Light Source.—For the visible and up to wavelength 3400 A. a white light, such as that given by a half-watt or Pointolite lamp, can be used, but between 5000 A. and 2100 A. the condensed spark is the most generally useful. Suitable electrodes for the spark can be prepared as follows: Carbon rods about 15 mm. long and 4 mm. diameter are filed to a wedge shape at the ends and boiled in a strong solution of uranium nitrate, after which they are dried and heated to redness. This process is repeated three times. They are then boiled in a strong solution of ammonium molybdate and again heated, this also being repeated three times. They are then ready for use. They should be mounted in their holders with the edges of the wedge parallel to, and in line with, the axis of the collimator. These electrodes, due to H. C. Jones, of Baltimore, are referred to as "Jones electrodes" (F. 132).

Other sources recommended by various workers are the iron arc, a spark between iron and nickel, and the cadmium spark or arc. The last is stated to possess the especial advantage of giving a continuous back-

ground between the strong lines, and thus to furnish a good means for the observation of sharp and narrow bands. Still better, it is stated, for

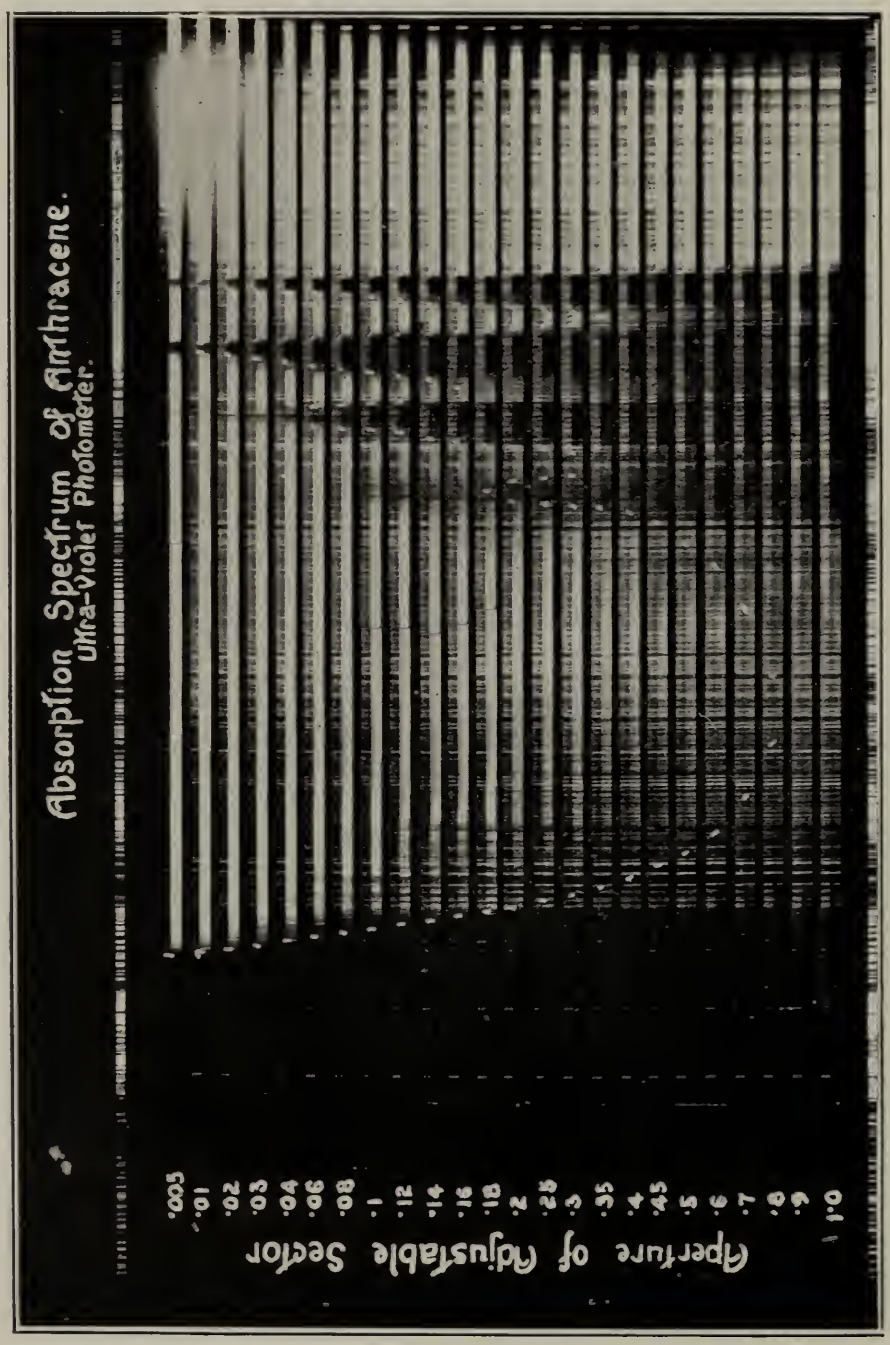
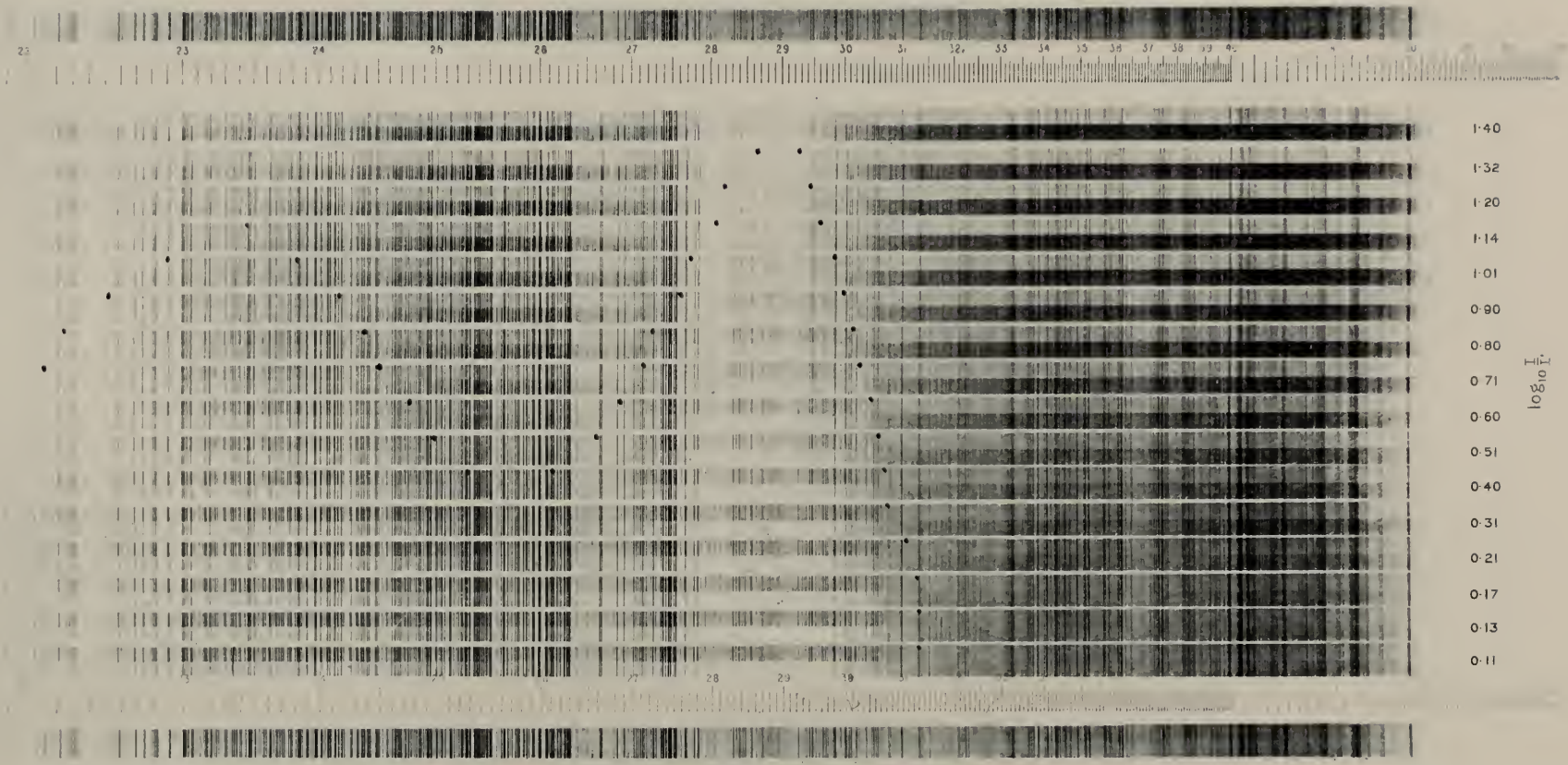


Fig. 3.

certain work is a Tesla discharge between aluminium electrodes under water, though this arrangement has been found by us troublesome to



ABSORPTION SPECTRUM OF URIC ACID SOLUTION 1 IN 100,000 IN 2 CM. THICKNESS
TAKEN BY MEANS OF A SECTOR SPECTROPHOTOMETER.

keep in good condition. For a comparison spectrum the copper arc, or for the far ultra-violet the aluminium spark is convenient.

For the arc, see catalogue items F 4, F 127, F 129, and F 284; and for the spark, items F 3, F 281, F 282, F 283, F 284, and F 285.

Spectrograph.

The instrument to be recommended for the photographic study of absorption spectra is the E 3, a quartz spectrograph with wavelength

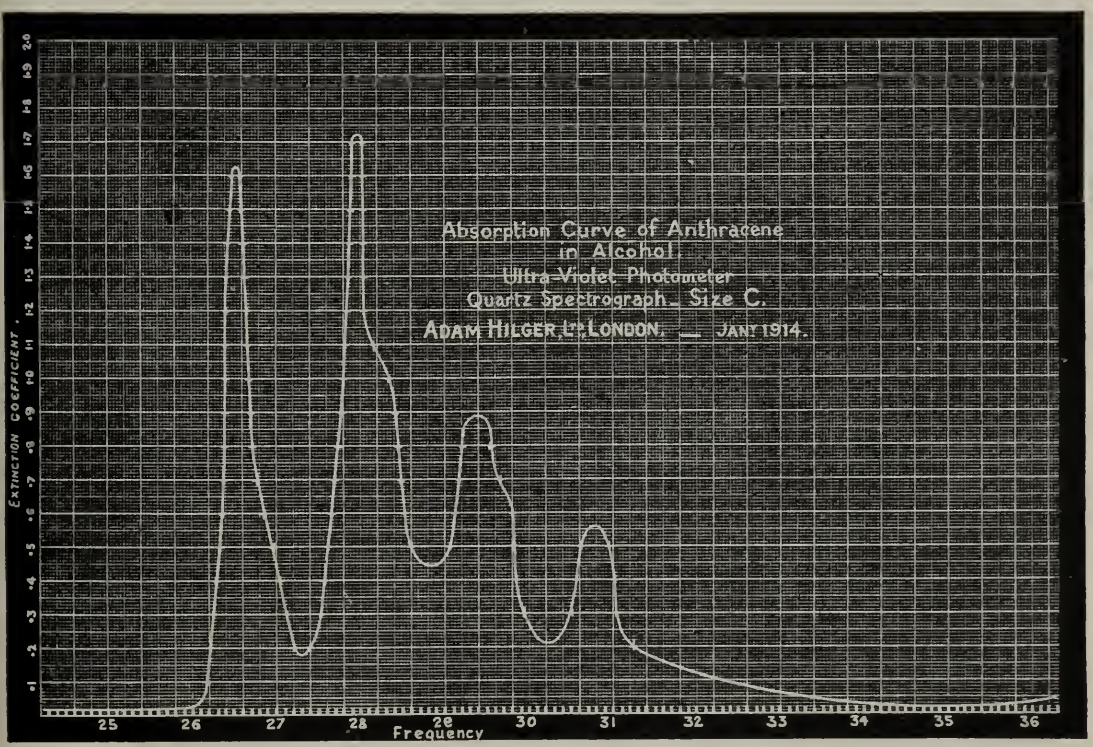


FIG. 4.

scale, to which for quantitative work should be added the Sector Photometer H 16 with suitable absorption tubes H 17.

In cases where accuracy of wavelength measurements is not so important the small quartz spectrograph E 37, which has a dispersion about one third of that of the E3, can for absorption work be used instead of the latter instrument with equally good results.

Sector Spectrophotometer.

Fig. 3, obtained on a Hilger Quartz Spectrograph E 2 (the same as the E 3, but without the wavelength scale) with sector photometer H. 16,

and Fig. 4, the curve drawn from it, show in the case of anthracene the method of drawing quantitative absorption curves.

This apparatus and its use are fully described elsewhere,[1] and it suffices here to say that the process of taking a quantitative absorption spectrum consists in taking on one and the same plate a series of photographs (see Fig. 3). Each strip consists of a pair of spectrograms closely juxtaposed, each pair consisting of two spectra of the light source, the one reduced in intensity by the action of a sector of variable but known aperture in the path of light ; the other by passage through the medium whose absorption is to be measured. Thus one photographic plate contains all that is necessary for drawing the complete absorption curve (Fig. 4).

A new Sector Spectrophotometer has recently been designed and used by Dr. S. Judd Lewis, the construction and advantages of which are described by him in the *Transactions of the Chemical Society*, 1919, vol. 115, p. 312-319, and in his Cantor Lectures, p. 17-19. The photogravures of Pseudo-globulin and Uric Acid appearing opposite pages 15 and 27 were taken by Dr. Lewis, using this instrument as made by the licensees.[2]

The photograph relative to Pseudo-globulin shows only a part of a series of 50 spectra which cover 3 plates, with a view to critical examination of the absorption band. Thus the form of the depression at a wavelength of 2505 can be studied closely, as also the form of the downward sweep at wavelengths between 2900 and 3000.

That for Uric Acid exhibits selective absorption in the region of wavelengths 2800 to 3000, which is typical of several members of the purine group. It is characterised also by an absorption band having its head at wavelength 2350, and by a power of transmission at 2200, which is very considerable.

If the results obtained with these two forms of spectrophotometer be compared with the curves sketched by inspection in Hartley's method, it will at once be seen what an important new tool has now been placed in the hands of organic chemists.

[1] Catalogue Section E, and *Spectrophotometers*, Adam Hilger Ltd.

[2] See p. 74.

SECTION III

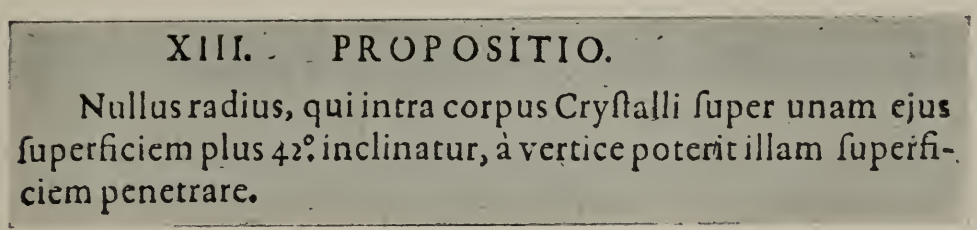
THE REFRACTOMETER

ALTHOUGH the work of Gladstone and Dale, and later of Brühl and Landolt, leading to the concepts of molecular and atomic refraction has been of great value in arriving at conclusions relative to constitution, it is undoubtedly true to-day that the chief uses of refractometry lie in purely empirical fields, such as the identification of substances, control of manufacture, estimation of mixtures, etc. It is these latter applications with which this booklet deals.

Modern refractometers of the Abbe and Dipping type require no knowledge of optics for their manipulation, but a few brief historical notes will not be out of place, even in a brochure primarily devoted to an account of practical applications.

Historical Notes.

The Abbe and Dipping Refractometers depend upon the observation of the critical angle of total reflection. The phenomenon of the critical


XIII. PROPOSITIO.

Nullus radius, qui intra corpus Cryſtalli ſuper unam ejus ſuperficiem plus 42° inclinatur, à vertice poterit illam ſuperficiem penetrare.

FIG. 5.

angle was probably known very early in the history of Optics, but the first mention of it yet traced is in Kepler's *Dioptrice*, published in 1611. Here he states (Prop. xiii. p. 4) that a ray incident on the surface of a " crystal " cannot pass out of it, if the ray makes an angle greater than 42° with the normal to the surface.

A photographic reproduction from a copy of Kepler's *Dioptrice* in the British Museum is given above (Fig. 5). This original Latin

edition of Kepler's book is very scarce, but a German translation has been made by Plehn (No. 144, Ostwald's Klassiker, Engelmann, Leipzig).

The famous Sine Law of Snell was not discovered till about ten years afterwards. Although this was not published until the appearance of Descartes' *Dioptrique* (Leyden) in 1638,[1] even then it was left to Sir Isaac Newton to state the simple corollary that since

$$\frac{\sin i}{\sin r} = \frac{1}{n} \text{ for light emerging from denser body,}$$

$$\sin i = \frac{1}{n} \text{ when } r \text{ is a glancing angle of } 90°.$$

The first to realise the possibilities of this property as a practical method of measuring the refractive index of a substance was Wollaston, who in 1802 (*Phil. Trans.* **92**, 365) made the first critical angle refractometer, which embodied the principle of the right-angled prism later adopted by Pulfrich.

With the difference that he used "sights" instead of a telescope with cross-lines, and a link motion giving the refractive index on a linear scale instead of using a graduated circle, Wollaston realised the most important principles of the modern refractometers, and succeeded in making an instrument giving results correct to the third place of decimals —a remarkable achievement considering the limited resources for optical and mechanical manufacture in those days.

Wollaston also applied his method for determining the indices of opaque bodies; and, in the case of oil of cloves, actually used his refractometer to detect falsification.

Wollaston must then be considered the originator of Critical Angle Refractometry.

Apparatus.

Particulars of the various types of refractometers may be derived from the catalogues of the publishers as follows:—

Abbe refractometer; see section M.
Dipping refractometer; see separate leaflet.
Pulfrich refractometer; see section M.
Rayleigh Interference refractometer; see section M.

The following data will afford a first indication of the instrument to be selected.

[1] Descartes, *Dioptrique*. Discourse second.

Ranges and Sensibilities of the Different Types of Refractometer.

	Range, n_D.	Sensibility.
Abbe Refractometer - -	1·3000 to 1·7000	0·0001
Dipping Refractometer -	1·32539 ,, 1·36640	0·00004
Pulfrich Refractometer - -	1·3300 ,, 1·7300	0·00005 (dispersions to 0·00002)
Rayleigh Liquid Refractometer	0·0063	0·0000021 (using a 1 cm. cell)
Rayleigh Gas Refractometer -	0·000018	0·00000018 (using 100 cm. tubes)

Scientific Aspects.

In spite of numerous papers that have followed each other for many years on the subject of atomic and molecular refractions, no final agreement has yet been reached as to the values to be assigned to atomic refractions under all conditions of linkages. Thus, Steiger (Berichte, (1921), 54, (B) 1381), departs from the principles laid down by Brühl, and calculates separate refraction constants for the different linkages, while giving constant values to the atoms. The single bond between two carbon atoms, or between one carbon and one hydrogen atom, was found to be different in the aliphatic and aromatic series.

Eisenlohr, who is author and part author of the only two books devoted to molecular refraction has broken with tradition in three papers, published in the *Berichte* during 1920 and 1921, and finds that the simple expression $M \times n_D^{20}$ "the molecular co-efficient of refraction," is more sensitive to changes of constitution than the old molecular refraction. It is still necessary, however, to make special hypotheses to explain abnormalities. The elimination of density, as Eisenlohr points out, makes the expression more sensitive, for density and refractive index usually vary in the same sense.

The superiority of the refractive index over the specific refraction for detecting changes during neutralisation in solution was already well known (Cornec, *Ann. Chim. Physique* (1913), 29, p. 490). Alkali Hydroxides were neutralised by polybasic acids, when the refractive index curves showed marked breaks at the points corresponding to the different salts formed, while in the curves of specific refraction, the salt formation was much less striking.

The important papers by Heydweiller and his associates on the refraction, dispersion and ionisation of salt solutions, published in *Wiedemanns Annalen*, 1912 and 1913, have not yet received adequate discussion. Apart from their theoretical significance the papers contain measurements of many salts at different concentrations, which would be valuable to the technical chemist.

In the space available it would be impossible to refer even by title to all the recent papers of importance, but the reader interested in problems of atomic refraction, may be referred to Silberstein's two papers in the *Philosophical Magazine* of 1917, obtainable in pamphlet form from the publishers of this brochure.

Applications of the Refractometer.

F. Löwe (Chemiker Zeitung, **45**, 25-27 (1921)), remarks that it is surprising how many graduates in chemistry enter industry without any knowledge of technical refractometric methods, although, at least in Germany, a Refractometer is generally provided in factory laboratories, and in State laboratories where food and drugs are analysed.

The introduction of the Abbe Refractometer and later of the Immersion or Dipping Refractometer facilitated greatly the introduction of refractometric methods of analysis, since the earlier Pulfrich—accurate though it is—is not very convenient for a number of consecutive determinations. The Pulfrich in its turn had been a great improvement on the spectrometer, which was employed by Gladstone and the earlier workers.

The firm of Carl Zeiss of Jena showed great enterprise in attempts to popularise the Abbe and the Dipping Refractometers. Well-known workers in different industries were encouraged to use the instrument for purposes of control. Valuable additions to the literature of the subject have been published as a result. Not less important are the English and American investigations associated with the names of Parry, Pickering, Harvey and Wilkie, Simmonds, Leach, Lythgoe, Trim, Fryer and Weston, Sheppard and many others.

B. Wagner, who commenced a systematic study of refractometric determinations of dissolved substances in his Dissertation, Jena, 1903, extended this work by the publication of his well-known Tables, 1907.[1] This book is a most important manual for aqueous solutions within the range of the Dipping Refractometer. If all the scattered publications of similar tables could be collected and collated with Wagner's work, a

[1] See p. 74.

very valuable book of reference would be produced. Adam Hilger Ltd. have been collecting data on this subject for a considerable time and intend to publish this information in a readily available form. In technical organic chemistry comprehensive collections of published data and of original measurements are contained in the books on Fatty Oils by Lewkowitsch, Fryer and Weston and Pickering, while Parry and Schimmel have rendered similar services for the Essential Oils.

Adam Hilger Ltd. have published two volumes on Refractive Indices, containing complete literature references, which are the only collections of this kind hitherto published, Volume 1, Refractive Indices of Essential Oils ; and Volume 2, Refractive Indices of Oils, Fats and Waxes. These data were compiled by R. Kanthack and edited by J. N. Goldsmith.

Here we would enter a plea for assistance in this publication of lists of Refractive Indices. Many chemists must possess records of determinations which would be of great value if accessible to other workers. Once extensive tables are in existence, it is probable that the Refractometer will in many cases displace with advantage the Hydrometer and Pyknometer. The publishers will be pleased to acknowledge any observations, and to publish them if possible in their series of tables of Refractive Indices.

The Butter Refractometer and its uses are too well known to need more than a passing reference. Since 1898 it has been an official instrument for butter testing in Germany.

The interest in refractometrical analysis was well shown at a largely attended meeting of the Society of Chemical Industry on February 3, 1919. Mr. Main described the use of the instrument in sugar works. Dr. Annie Homer gave the method employed in the determination of the protein content of anti-toxin sera with the immersion instrument, and Mr. Berry spoke of the analysis of ethylene-chlorhydrin by the Abbe instrument. The papers were followed by an interesting discussion on refractometrical analysis. It was evidently the opinion of the meeting that the instrument was capable of greatly extended use.

The Refractometer has been applied to a considerable extent in the last few years to the study of Petroleum and its products, and a selection of values, which are a guide to further work, may be found in the Treatise of Engler-Höfer. Most of the work has been done on American Petroleums, and data, particularly for East India products, are still incomplete.

Caution must be exercised in drawing inferences from Refractometer readings of unknown Petroleums, yet if sufficient information is available

as to the nature of the mixture, an analysis can be made with extraordinary ease ; for instance, a mixture of Petroleum Spirit and Benzol may be rapidly analysed. (Appendix, pp. 44 to 46.)

It is gratifying to see that dispersion measurements are finding a technical application here as elsewhere, *e.g.* Darmois (Compt. Rend. (1920), 171, 952), for this property has been somewhat neglected by technical chemists, although a measurement of Dispersion merely involves two measurements of Refractive Index or one reading of the Abbe.

Main introduced the use of the Abbe Refractometer into the sugar industry for determining the sugar content or total solids, and his work has been followed by numerous publications, so that the Refractometer is now well established as a routine instrument in that industry. Schönrock, of the Physikalisch-Technische Reichsanstalt (Z. Ver. Deut. Zuckerind. **61**, 421), prepared a similar table to Main's, and the earlier worker's figures were confirmed throughout, while a similar agreement is shown by Wagner's Sugar Tables. The handbooks on sugar analysis, such as Browne's, reprint these tables and also tables of temperature corrections.

It was evident that the refractometer would be applicable in the fermentation industries, and there are many papers describing the refractometric determination of extract in beer and wine, while intermediate products, such as worts and mash, have also been analysed in this way. The variety of the information yielded by the instrument in these industries has, indeed, surpassed expectations, for its use has greatly shortened the determination of Ethyl Alcohol in the presence of the higher Alcohols for Excise purposes, while as regards Beer, the percentage of Alcohol and Extract can be obtained and the original gravity deduced after the Specific Gravity and Refractive Index have been determined. Mixtures of Methyl and Ethyl Alcohol may be very rapidly analysed by the Dipping Refractometer, and this determination is of particular interest, for the Specific Gravities of the two Alcohols diverge much less than their Refractive Indices. A full description of these methods and the necessary tables are contained in " Alcohol," by C. Simmonds.

The estimation of Starch in potatoes and cereals has been thoroughly studied, and provided definite conditions are adhered to, yields results that are not inferior to Polarimetric methods. The Starch is converted into sugar, and since the Refractive Indices of the soluble starch, maltose,

dextrose, etc., are practically the same, the Starch percentage may be calculated without a knowledge of the proportion of the different sugars present. A review of this subject is given by F. Löwe (Chem. Zeit. **45**, 25-27 (1921)).

Much work has been done on the application of the Refractometer to Milk examination, notably the determination of added water. Ackermann, whose name is well known in connection with the refractometric analysis of Beer, has standardised a method for the determination of water in Milk, which was confirmed by Mai and Rothenfusser, who analysed 5,000 samples in this way.

One or other of the different types of Refractometers or Rayleigh Interference Refractometers (briefly called Interferometers) have been used from time to time for following the course of reactions, or for measuring the approach of a mixture to the point of equilibrium or saturation ; for instance, Svedberg's work on adsorption. The advantages of this method are clear, for only a very small quantity of the liquid is withdrawn for examination, or, alternatively, the Dipping Refractometer may be immersed in the liquid without alteration of its composition. Any desired degree of sensitiveness may be obtained by substituting the Dipping Refractometer for the Abbe, or the Interferometer for the Dipping Refractometer.

The Dipping Refractometer can be used as a portable instrument for the control of factory processes and can easily be arranged to dip into a tank, so that it can be used as readily as a Hydrometer. The temperature must, of course, be ascertained at the same time. End points of reactions can be determined in this way ; for instance, when a precipitating solution of higher Refractive Index is added to a liquid to produce a precipitate, the Refractive Index of the mixture falls with each addition of the precipitant, until the end point is passed, when further additions of the precipitant cause an increase of Refractive Index. The end point is obtained with considerable approximation by plotting, say, five readings.

In following the course of a reaction by means of the Dipping Refractometer it is not always necessary to adhere rigidly to the directions hitherto published. If the object of the experiment is to control a technical operation where differential readings suffice, and the solutions are at room temperature, a bath or thermostat may be dispensed with. Care should, of course, be taken not to alter the temperature of the solutions or prisms by handling them. No one would attempt to determine refractometrically

the end point of a reaction for which senstive indicators are available, yet the end point of any precipitation reaction may be found with the instrument in the way described, and smooth curves are obtained with a sharp turning point.

The Refractometer may be dipped into a beaker standing on a mirror, and containing the liquid to which the precipitant is being added from a burette. If the precipitate settles readily, readings are obtained at once, but if a finely divided precipitate is formed, which settles slowly, a sample may be withdrawn into a small auxiliary beaker from time to time, or preferably a drop may be removed with a thermometer or stirring rod and placed on the auxiliary prism, a bath is required in this instance.

Since the physical properties of colloid solutions have been studied so intensively during the last few years, it was evident the Refractometer would be applied to the problems of Colloid Chemistry. It has been found that the degree of dispersion is practically without effect on the Refractive Index (Kolloid Zeit. (1920), 10-15), although it is of interest to note that the effect of temperature on the refraction of Gelatine Solutions is peculiar, in that the specific refraction by either of the two well-known formulae varies very much with temperature, while only slight variations were found with the sols of Stannic Acid, Silicic Acid, Arsenic Sulphide, etc.

It may be mentioned here that if an oil is emulsified in Soap Solution the Refractometer will show the Refractive Index of the continuous phase, *i.e.* the Soap Solution (Goldsmith, J., Oil and Colour Chem. Assn., March 1921).

Attention should be called to a series of papers by Zwick, which appear in the Deutsche Gerber-Zeitung (1908), and by Sager in Collegium (1909), on the estimation of Tannin by the Refractometer.

Since the Dipping Refractometer and the Interferometer are used regularly for the estimation of Salts in sea-water, it is evident that these instruments could be used in tidal waters of rivers where the determination of the degree of penetration of sea-water is required. Further, the Interferometer would be very useful to Authorities concerned with river pollution, for even the small alteration of the total solids due to the discharge of effluents from factories or towns can be detected and measured very rapidly.

A number of chemical substances of importance have been measured by Utz, and the tables published in different journals as follows :—

Cresol Soap, " Lysol " (Apoth. Zeit. (1906), 763).
Camphor (Allgem. Chem. Zeit. (1896), 987).
Alkaloids and Glucosides (Chem. Zeit. (1909), 47).
Formaldehyde (Chem. Zeit. (1906), 982). (A Formaldehyde Table is contained in Wagner.)

Caffeine was measured by Hanus (Z. Unters. Nahrungs u. Gennussm. (1906), **2**, 313). Glycerine has been measured by a number of authors including Wagner (0 – 28.72%) and Skalweit (0 – 100%), and also by Wolff (Zeit. angew. Chem. (1919), **32**, 148).

The preparation of tables or curves for any specific purpose is, of course, a simple matter and well worth undertaking by anyone requiring to make frequent determinations of the same kind.

In a recent paper [1] on the refractometer some of the industrial applications of the instrument have been well summarised as follows :—

1. Acetic acid, carbolic acid, cresylic acids, and other organic acids.
2. Sulphate of ammonia, nitrate of potash, and numerous other inorganic salts in solution.
3. Ammonia.
4. Acetone, alcohol, and many other organic solvents.
5. Glycerine, formalin, nicotine, pyridine.
6. Essential oils, and the terpenes. (Turpentine and its substitutes.)
7. Fatty oils, fats, and waxes, and also fatty acids and by-products.
8. Mineral oils and waxes and products of distillation derived from them.

To the above may be added sugar, resins, benzol, toluol, solvent naphtha, and organic liquids generally. Among the substances for the determination of which tables exist, nicotine and pyridine can now be included. The Abbe has recently been used for the determination of Paraffins in Tar Oils.

For creosotes the refractometer test is likely to become of considerable importance. In the preservation of timber it is only the coal tar and coke oven creosotes which are of high value, the blast furnace and water gas tar creosotes being deficient in those constituents which are preservative. It has recently been shown by Messrs. Dean and Bateman (Circular 112 of the United States Forest Service) in a paper on the Refractive Index of Creosotes, that the refractometer forms a test for

[1] " The Use of the Refractometer in Chemical Industry," by Percival J. Fryer, F.I.C. *The Chemical Age* (March, 27 1920), 326.

distinguishing coal tar and coke oven creosotes from blast furnace and water gas tar creosotes; and the experiments and conclusions of Dean and Bateman have recently been verified independently in this country.

It will be seen that there are few chemical industries in which the refractometer is not already well established as an approved means of test in control of manufacture or examination of raw materials or of products. It is not surprising, therefore, that one of the newest industries, fat-hardening, is controlled by measuring refractive indices instead of iodine numbers.

A further industrial application of the refractometer is described in the paper by Fryer [1] and we quote this *in extenso*. Having referred to the main use of the refractometer in industry, the writer points out a further novel application to works control, which he has used for a considerable time in the works with which he is associated. He says, " It applies to mixtures of liquids or solutions which form a viscous or semi-solid product, and in which it is difficult to ensure a uniform dissemination of all the constituents throughout the entire bulk of a batch of material.

" Many manufactured products are of this nature, and it is usually very necessary to know if, and when, adequate mixture of the constituent materials has taken place. In some cases this is extremely difficult to determine with any degree of certainty, especially in the case of complex mixtures, when even chemical analysis would probably fail to yield conclusive results, and would, in any case, be too slow a method for works' control. In such instances the refractometer will prove of great assistance when used in the following manner :

" Samples are taken from different portions of the batch of material, say, at the top, bottom and middle of the vessel, and examined in the refractometer. If the figure, whatever it may be, is identical in all the samples, there is a strong indication that a homogeneous product has been obtained, and it can be assumed that the mixing has been efficient. If, on the other hand, the samples differ, there is an indication of local excess of one or other of the constituents, proving that the mixing has been inadequate. The reading on the instrument may even be indistinct providing that it is equally so in each sample. Of course, the best control is obtained by this method when the refractive power of the different ingredients used varies to a considerable extent, and in industrial products this will be found to be very frequently the case.

[1] See footnote to p. 37.

"An example from the writer's own observations may be given. It is known that soap gives a fairly definite reading on the Abbe Refractometer, the figure varying with the strength (fatty acid percentage) of the soap. In mixing compound insecticides, of which nicotine is frequently an ingredient, it is often a difficult matter to know when such insecticides have been efficiently dissolved or distributed in the soap. If, however, samples are taken and examined as described above, the mixing is readily controlled in a perfectly satisfactory manner."

The Refractometer in Physiological and Clinical Analyses. (See Appendix II.)

The refractometer has also been extensively used in physiological and clinical analyses. There are many references in Abderhalden's *Handbuch der biochemischen Arbeitsmethoden*, especially vol. i. pp. 568-583.

The ordinary Dipping Refractometer has a scale from n_D 1·32539 to 1·36640, and reads by estimation to 0·01 of its scale division, corresponding to an uncertainty of 0·000004 in n_D. Reiss employed this instrument for the determination of the protein in blood serum, in which it can be rapidly estimated on a few drops with an error of 0·2 per cent. Many other clinical uses were introduced by H. Strauss (stomach contents), by A. Strubell, J. A. Grober, and others (urine).

In vol. 8 pp. 84-119 of Abderhalden's *Handbuch* particulars are given of refractometric studies of blood serum, fibrinogen determination, secretions and exudations, cerebrospinal liquid, stomach contents, milk, and the action of ferments and bacteria. Brailsford Robertson's method of serum analysis with the refractometer determines total non-protein, globulin, and albumen.[1]

The Pulfrich Refractometer.

This instrument gives a higher accuracy than the Abbe, and also has a longer range (from 1·33 to 1·73), if both the interchangeable prisms are supplied. It is for these reasons that this instrument is generally employed for determining the refractive indices of glass and liquids where a greater accuracy than the Abbe is needed simultaneously with a wider range than the Dipping. For accurate measurements of Dispersion this instrument is superior to the Abbe.

[1] B. Robertson, *Physical Chemistry of the Proteins* (1918), pp. 60-66 with 34 references to original papers.

The Rayleigh Interference Refractometer, sometimes called the Löwe Refractometer again widens the possibilities of application of refractometry to chemical analyses. Many problems require a greater accuracy than can be obtained with the Abbe, the Dipping, or the Pulfrich Refractometers. In such cases the Rayleigh Refractometer for liquids, or the Rayleigh gas refractometer, as the case may be, is indicated.

One typical application of the former instrument is the determination of a sodium salt when present as an impurity in the corresponding potassium salt. By ordinary chemical methods, this is a laborious process, but with the Rayleigh Refractometer for liquids it is a matter of a few minutes only. A change from a 5 per cent. solution of potassium chloride to a 5 per cent. solution of sodium chloride gives, with careful working, 600 measurable units. Therefore, in a solution of 5 per cent. of the mixed salts an accuracy of 0·2 per cent. can be attained.

A novel use of the Interferometer has been made by three American authors, who employ the instrument to measure the compression of water and hence by suitable connections to measure the osmotic pressure of a sugar solution (*J. Amer. Chem. Soc.* (1921) 2497).

The same type of instrument when arranged for gases (the Rayleigh gas refractometer) has of late years become of considerable importance in gas analysis. In this connection it is valuable in laboratories of chemical works manufacturing pure compressed gases, and in those requiring to control the composition of intermediate product gases, in Public Health offices and medical institutes for the systematic analysis of air, and in refrigeration works ; also in mines, in gas works, and to control the permeability of balloon and airship fabrics.

Ultra-Violet Refractometer.

This apparatus for measuring refractive index and dispersion for the ultra-violet rays has as yet no industrial applications. Particulars will be found in section M of the publishers' catalogue.

Intending purchasers of a refractometer would do well to mention to the maker the chief purpose for which it is intended to use it. In some cases the Abbe, and in others the Dipping (*i.e.* immersion) refractometer, in others again the Pulfrich or Rayleigh Interference instruments may be the most useful.

List of Books Dealing with the Practical Applications of the Refractometer.

Leach. *Food Inspection and Analysis*, 1913. Chapman and Hall.

Lewkowitsch. *Oils, Fats, and Waxes*. Macmillan.

Fryer and Weston. *Oils, Fats, and Waxes*, vol. ii. Cambridge University Press, 1918.

Roth und Eisenlohr. *Refraktometrische Hilfsbuch*. Leipzig, 1911.

E. J. Parry. *Chemistry of the Essential Oils*. Scott, Greenwood.

Allen. *Commercial Organic Analysis*. Churchill, 1911.
Vol. i., pp. 22, 126, 316.
Vol. ii., p. 291.
Vol. iv., pp. 243, 253.

Simmonds. *Alcohol*. Macmillan, 1919.

Abderhalden. *Biochemische Arbeitsmethoden*.
Vol. 1, p. 582 : Generalities.
Vol. 8, p. 84-119 : Pathological Applications, etc.

Sidersky. *La Réfractométrie*. Paris, 1909.

APPENDIX I

List of Substances in Solution for which Wagner gives Tables of Dipping Refractometer Readings.

In the case of each substance the Dipping Refractometer reading is given over a considerable range of concentrations.

Hydrochloric, nitric, sulphuric, phosphoric, boric, chromic, and perchloric acids.

Potassium and sodium hydroxides.

Ammonium, potassium, sodium, barium, calcium, strontium, ammonium, magnesium, ferric, mercuric, gold, and platinum chlorides.

Potassium, sodium, and ammonium bromides.

Potassium and sodium iodides.

Potassium chlorate.

Potassium, sodium, silver, and barium nitrates.

Potassium, sodium, ammonium, magnesium, zinc, copper, ferrous, and aluminium sulphates.
Potassium-aluminium, nickel, and manganese sulphates.
Sodium sulphite.
Sodium bisulphite.
Sodium thiosulphate.
Potassium and sodium carbonates.
Potassium and sodium bicarbonates.
Sodium phosphate.
Sodium borate.
Potassium chromate.
Potassium bichromate.
Ammonium sulphocyanate.
Formic, acetic, oxalic, lactic, tartaric, and citric acids.
Potassium, sodium, ammonium, and lead acetates.
Potassium oxalate, potassium binoxalate.
Methyl alcohol, ethyl alcohol.
Glycerine, formaldehyde.
Cane sugar, dextrose and other sugars.
Phenol, sodium salicylate, tannin.

Furthermore, special methods of determination are given for calcium, magnesium, and phosphoric acid.

APPENDIX II

PRINCIPAL APPLICATIONS OF THE REFRACTOMETER TO BIOCHEMICAL METHODS REFERRED TO IN ABDERHALDEN, *Biochemische Arbeitsmethoden.* Vol. I, p. 582.

A. STRUBELL. "Über eine neue Methode der Urin und Blutuntersuchung." Verhandlungen des XVIII Kongress für innere Medizin zu Wiesbaden, 1900. Deutsches Archiv für klinische Medizin. Vol. lxix. p. 521 (1901).

E. REISS. "Eine neue Methode der quantitativen Eiweissbestimmung." Archiv für experiment. Path. u. Pharmakol. (1904), **51**, 18. "Der Brechungskoeffizient der Eiweisskörper des Blutserums." Hofmeisters Beitrage zur chemischen Physiologie und Pathologie (1904), **4**, 150. "Klinische Eiweissbestimmungen mit dem Refraktometer." Verhandlungen der LXXVI Versammlung Deutscher Naturforscher und Arzte zu Breslau (1904), **2**, 35. "Anwendungen der Refraktometrie

in der Physiologie und Pathologie des Menschen." Bericht über die XV Hauptversammlung der Deutschen Bunsengesellschaft für angewandte physikalische Chemie (1908), **14**, 613.

If a solution of constant refractive index contains varying amounts of a second substance, this substance may be determined by the refractometer. The work of E. Reiss on blood serum is an instance of this problem. Blood serum from this point of view is a solution of varying quantities of protein in a liquid whose refractive index is constant or only subject to very small variations.

If the refractive index of the protein-free liquid $=n$, *that of the serum* $=n'$, *then according to the table constructed by Reiss the protein content of the serum may be read off from the difference* $n' - n$, *the average error is* 0·2 *per cent. protein. Since the analysis requires only a few drops of blood, this refractometric method is of great clinical importance.*

H. Strauss. "Demonstration der refraktometrischen Blutuntersuchung." Deutsche med. Wochenschr. (1905), Nr. 2.

H. Strauss und B. Chajes. "Refraktometrische Eiweissbestimmungen an menschlichem Blutserum und ihre klinische Bedeutung." Zeitschr. f. klin. Med. (1904), **52**, Heft 5 und 6.

K. Martins. "Vergleichende Untersuchungen über den Wassergehalt des Gesamtblutes und des Blutserums." Folio hæmatologica (1906), Jg. **3**, Nr. 3.

H. Strauss. "Über den Brechungsexponenten von Mageninhalten." Deutsche Arzte-Zeitung (1901), Heft 4.

J. A. Grober. "Quantitative Zuckerbestimmung mit dem Eintauchrefraktometer." Zentralbl. f. innere Med. (1900), **21**, 201.

E. Riegler. "Die Refraktometrie des Harns im Dienste der Medizin." Atti del VI. Congresso internazionale di chimica applicata (Rom, 26 April bis 3 Mai 1906), **5**, p. 167 (Rom, 1907). Bericht in der Zeitschr. f. angewandte Chemie (1906), Jg. **19**, 918.

H. O. G. Ellinger. "Optische Bestimmung der Albuminmenge im Harn. Journ. f. praktische Chemie" (1891), 2 Reihe, **44**, 256.

H. Strauss und J. Leva. "Über eine neue Form der Motilitätsprüfung des Magens." Deutsche med. Wochenschr (1907), Nr. 29.

Gerhard Schorer. "Über refraktometrische Pepsinbestimmungen." Dissertation. Bern 1908.

Reference should also be made to

J. Bečke, Zeit. physiol. Chem. (1922), vol 121, 228. Analysis by Refractometer and Interferometer.

References to the Use of the Refractometer in Pathology and Food Analysis.

"Methods of Refractometrical Investigation in Biology," by E. Reiss. Abderhalden's *Arbeitsmethoden*, vol. 8. pp. 84-119.

Contents :

1. Abbe refractometer.
2. Milk fat refractometer.
3. Dipping refractometer.
4. Blood serum.
5. Estimation of fibrinogen.
6. Estimation of volume of blood corpuscles.
7. Excretions and secretions.
8. Cerebro-spinal liquid.
9. Urine.
10. Stomach contents.
11. Milk.
12. Estimation of fat.
13. Testing blue solution of milk.
14. Testing milk serum.
15. Estimation of milk sugar.
16. Testing the action of ferments and bacteria.
17. Further applications

"Study of Protective Ferments with the Interferometer," by P. Hirsch, Abderhalden's *Arbeitsmethoden*, vol. 8, pp. 561-572.

APPENDIX III

Application of Temperature Corrections to Mixtures.

Too little attention has been given in the past to the accurate determination of temperature coefficients in refractometry, with the result that full advantage has not been taken of the accuracy of refractometers. Numerous attempts have been made to obtain temperature coefficients which can be applied indifferently to large classes of compounds. It must be remembered that any such rough and ready means of correction can only be applied where the working temperature is very near indeed to that taken as a standard. Every careful worker should ascertain the temperature coefficient of each substance in which he is interested.

Furthermore, where there is a case of determining considerable amounts of one substance in mixture with another, it is necessary for him to obtain the temperature coefficient for the particular mixture.

The trouble of preparing tables for the purpose is well repaid where the determination of a particular kind of mixture has to be frequently repeated.

As an example of such a table, we give on page 46 the refractive indices of various mixtures of petroleum spirit and benzol at different temperatures. This table has been prepared and is in use at a large chemical laboratory where work frequently requires to be done at high pressure. On this table the percentage by volume of petroleum in the mixture can be immediately obtained from the refractive index, as given on the Abbe Refractometer at any temperature from 10° to 30° C. This furnishes a ready means of sorting out samples. It is more expeditious than distillation or specific gravity determinations, and requires very little liquid.

REF. IND. OF MIXTURES OF PETROLEUM SPIRIT AND BENZOL.

A	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20° C	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°	A
0	—·0062	·0056	·0050	·0043	·0037	·0031	·0025	·0019	·0012	·0006	1·4978	+·0006	·0012	·0019	·0025	·0031	·0037	·0043	·0050	·0056	·0062	0
5	—·0062	·0056	·0050	·0043	·0037	·0031	·0025	·0019	·0012	·0006	1·4922	+·0006	·0012	·0019	·0025	·0031	·0037	·0043	·0050	·0056	·0062	5
10	—·0061	·0055	·0049	·0043	·0037	·0031	·0025	·0018	·0012	·0006	1·4865	+·0006	·0012	·0018	·0025	·0031	·0037	·0043	·0049	·0055	·0061	10
15	—·0061	·0055	·0049	·0043	·0036	·0030	·0024	·0018	·0012	·0006	1·4808	+·0006	·0012	·0018	·0024	·0030	·0036	·0043	·0049	·0055	·0061	15
20	—·0061	·0055	·0049	·0043	·0036	·0030	·0024	·0018	·0012	·0006	1·4752	+·0006	·0012	·0018	·0024	·0030	·0036	·0043	·0049	·0055	·0061	20
25	—·0060	·0054	·0048	·0042	·0036	·0030	·0024	·0018	·0012	·0006	1·4697	+·0006	·0012	·0018	·0024	·0030	·0036	·0042	·0048	·0054	·0060	25
30	—·0060	·0054	·0048	·0042	·0036	·0030	·0024	·0018	·0012	·0006	1·4641	+·0006	·0012	·0018	·0024	·0030	·0036	·0042	·0048	·0054	·0060	30
35	—·0060	·0054	·0048	·0042	·0036	·0030	·0024	·0018	·0012	·0006	1·4588	+·0006	·0012	·0018	·0024	·0030	·0036	·0042	·0048	·0054	·0060	35
40	—·0060	·0054	·0048	·0042	·0036	·0030	·0024	·0018	·0012	·0006	1·4535	+·0006	·0012	·0018	·0024	·0030	·0036	·0042	·0048	·0054	·0059	40
45	—·0059	·0053	·0047	·0041	·0035	·0030	·0024	·0018	·0012	·0006	1·4483	+·0006	·0012	·0018	·0024	·0030	·0035	·0041	·0047	·0053	·0059	45
50	—·0058	·0052	·0046	·0041	·0035	·0029	·0023	·0017	·0012	·0006	1·4430	+·0006	·0012	·0017	·0023	·0029	·0035	·0041	·0046	·0052	·0058	50
55	—·0058	·0052	·0046	·0041	·0035	·0029	·0023	·0017	·0012	·0006	1·4377	+·0006	·0012	·0017	·0023	·0029	·0035	·0041	·0046	·0052	·0058	55
60	—·0057	·0051	·0046	·0040	·0034	·0028	·0022	·0017	·0011	·0006	1·4324	+·0006	·0011	·0017	·0022	·0028	·0034	·0040	·0046	·0051	·0057	60
65	—·0057	·0051	·0045	·0039	·0034	·0028	·0022	·0017	·0011	·0006	1·4272	+·0006	·0011	·0017	·0022	·0028	·0034	·0039	·0045	·0051	·0057	65
70	—·0056	·0051	·0045	·0039	·0033	·0028	·0022	·0017	·0011	·0006	1·4219	+·0006	·0011	·0017	·0022	·0028	·0034	·0039	·0045	·0051	·0056	70
75	—·0056	·0050	·0045	·0039	·0033	·0028	·0022	·0017	·0011	·0005	1·4168	+·0005	·0011	·0017	·0022	·0028	·0033	·0039	·0045	·0050	·0056	75
80	—·0055	·0050	·0044	·0039	·0033	·0028	·0022	·0017	·0011	·0005	1·4117	+·0005	·0011	·0017	·0022	·0028	·0033	·0039	·0044	·0050	·0055	80
85	—·0055	·0050	·0044	·0039	·0033	·0028	·0022	·0017	·0011	·0005	1·4067	+·0005	·0011	·0017	·0022	·0028	·0033	·0039	·0044	·0050	·0055	85
90	—·0055	·0049	·0044	·0038	·0033	·0027	·0022	·0016	·0011	·0005	1·4010	+·0005	·0011	·0016	·0022	·0027	·0033	·0038	·0044	·0049	·0055	90
95	—·0054	·0049	·0043	·0038	·0032	·0027	·0022	·0016	·0011	·0005	1·3968	+·0005	·0011	·0016	·0022	·0027	·0032	·0038	·0043	·0049	·0054	95
100	—·0054	·0049	·0043	·0038	·0032	·0027	·0022	·0016	·0011	·0005	1·3920	+·0005	·0011	·0016	·0022	·0027	·0032	·0038	·0043	·0049	·0054	100

Mixture of Benzol boiling from 75° to 82° (Specific gravity ·8835 at 15° ·5 C.), with petroleum spirit of same boiling range (Specific gravity ·7008 at 15° ·5 C.). Column A is percentage by volume of petroleum in the mixture.

To use table, take a reading at any temperature; read down the 20° column for the nearest readings, and put in the suitable correction. Thus, if actual reading is 1·4540 at 17° C., nearest readings are at 1·4535 and 1·4483, where the correction is —·0018, giving a reading corrected to 20° C. of 1·4522. This corresponds to a percentage between 40 and 45 of petroleum spirit in the benzol.

SECTION IV

THE POLARIMETER

This chapter is almost identical with that contributed by two of the present authors to Glazebrook's Dictionary of Physics, and is published here by permission.

Historical Notes.

The rotation of the plane of polarisation was first observed in the year 1811 by Arago in quartz plates. Biot, and also Seebeck, discovered the optical activity of some organic substances, Oil of Turpentine and solutions of Sugar and of Tartaric Acid.

Biot established the nature of the phenomenon and its laws in a long series of important papers which extend over a period of forty-seven years (1813 to 1860). One of his important experiments demonstrated that the vapour of Turpentine was optically active.

Fresnel published the theory of the properties of quartz and introduced the term " circular polarisation " in 1831.

W. Herschel and J. Herschel recognized the significance of certain faces on the quartz crystal for predicting the sign of the optical rotation.

An epoch-making discovery was Pasteur's in 1848. He proved in the case of Tartaric and Racenic Acids that one and the same active substance may occur in two forms, with opposite rotatory power, as well as in an inactive modification.

Pasteur stated that substances which are optically active as crystals or in solution crystallize in hemihedral forms ; *i.e.* the crystal and its mirror image cannot be superposed. (Pasteur's rule is not reversible, hemihedral crystals do not always rotate polarised light).

Pasteur thought that optical activity might be caused by a lack of symmetry of the entire molecule. When discussing the Tartaric Acids in 1865 (2) he explained his views in the following sentence : " Les atomes

de l'acide droit sont-ils groupés suivant les spires d'une hélice dextrorsum, ou placés aux sommets d'un tétraèdre irrégulier, ou disposés suivant tel ou tel assemblage dissymétrique déterminé ? "

No progress was made of theoretical importance until 1874, when Van t'Hoff and Le Bel, independently of each other put forward the celebrated theory that the optical rotation of organic compounds is due to the presence of an asymmetric carbon atom. They each assume that the four valencies of the carbon atom are directed to the points of a regular tetrahedron. If each of these valencies is attached to a different atom or radicle it is seen that two non-superposable tetrahedra result and these are the left- and right-handed forms of the active substance.

Thus the Polarimeter has played as celebrated a rôle in the development of theoretical organic chemistry as its essential parts, the nicol prism and the quartz plate, have done in theoretical optics.

The rapid progress of synthetical organic chemistry in the latter decades of the 19th century led to the study of a large number of new compounds which rotated polarised light.

One of the most celebrated of the prolonged researches connected with the Polarimeter was Emil Fischer's on the constitution of the sugars, in which the interpretation of optical activity played a prominent part.

Theoretically, optical rotation should arise from asymmetric valencies of elements other than carbon. Such predictions have been realised. We are now acquainted with substances whose rotation is due to asymmetric Nitrogen, Tin, Sulphur, Selenium, Phosphorus, Silicon, Chromium and Cobalt (3). English investigators, Pope, Peachey, Smiles, Neville and Kipping were chiefly concerned with the first six elements, while Werner was successful in obtaining the active compounds of Chromium and Cobalt.

The essential condition for the existence of two optical antipodes is now believed to be the absence of an axis of symmetry of the second order. Compounds are known possessing several asymmetric carbon atoms which are not resolvable into optical isomers. Conversely there are active bodies without asymmetric carbon atoms, their structural formulae, however, exhibit two possible arrangements with non-superposable images (Jaeger, *Rec. trav. chim. Pays-Bas*, 1919, (38), 371).

Besides these enquiries of fundamental importance, the Polarimeter was employed in a classical piece of research by Wilhelmy in 1850. He measured the rate of inversion of cane sugar and put forward the first correct mathematical treatment of the velocity of a chemical reaction.

The extraordinary convenience of analysing a solution by optical means without altering its composition was the motive for employing the instrument.

Magnetic Rotation of the plane of polarisation discovered by Faraday, was the subject of prolonged research by W. H. Perkin, Senior, who found that it was a property depending mainly on the constitution, although there are some additive relationships.

While the study of Rotatory Dispersion has prevented a too narrow interpretation being placed on the results with Sodium light a study of the influence of the solvents showed that not only the amount but also even the sign of the optical rotation could vary when the same substance was dissolved in different solvents.

Arising out of this purely scientific work is an interesting analytical method. The quantitative estimation of Benzene in cyclohexane is difficult and troublesome, but by taking advantage of the fact that Benzene is almost without influence on the rotation of Ethyl Tartrate, whilst cyclohexane exerts a considerable depressing influence, the proportions of Benzene and Cyclohexane present in a mixture may be estimated within about 3 per cent. by the simple determination of the rotatory power of a mixture with a fixed proportion of the Ester [4].

The influence of the solvent is also clearly shown in an important paper by F. H. Carr and W. C. Reynolds [5] on the rotatory power of alkaloids. They found, inter alia, that hydrastine has a strong dextro-rotation in 50 per cent. Alcohol and is lævo-rotatory in absolute Alcohol. These observations suggest that indirect determinations of inactive substances may often be possible, by measuring their influence on the rotation of an admixed active substance. It has been known for a long while that Boric Acid and also Acetone and other substances have a powerful effect on the rotation of Tartaric Acid. For the two substances mentioned, there are excellent chemical methods available ; where this is not the case a polarimetric method might well be looked for.

Applications.

The applications of the Polarimeter in the Sugar, Jam, etc., trades are too well known to require more than the briefest mention. Researches, particularly in America, are being carried out on the standardisation of the Saccharimeter, and in Germany on the preparation of a pure standard Sugar.

Starches can be determined by the Polarimeter by Ewen's method, and its later modifications; thus the products of another important industry may be controlled by this instrument. The relation between concentration and specific rotatory power has been determined for a number of substances with a very high degree of accuracy, particularly Cane Sugar, Galactose, Cocaine, Lactose, Maltose, Glucose, Camphor, and Nicotine.

A full account of the technique of the measurements followed by tabulated lists of the specific rotation of a large number of substances is contained in the standard work on the subject, Landolt's *Optical Rotations of Organic Substances and their Practical Applications.* It is to be hoped that this book will be brought up-to-date from time to time by publishing new editions. A second edition has been published recently.

"Synthetic Camphor" can be distinguished from Natural Camphor, and adulteration of inactive oils (such as almost all the fatty oils) with Rosin or Rosin Oil is easily detected. Castor Oil is the most important fatty oil possessed of optical activity, but the rotation varies too much for the property to be used in specifications and the same remark applies to French and American Turpentine.

Mineral Oils were thought for some years to be optically inactive, but further study has proved that they possess a small rotatory power, and this fact has supported one of the theories of the origin of Petroleum.

The temperature correction may be of great importance for the analysis of a mixture, thus a mixture of dextrose (+) and invert sugar (+ & −, the latter predominating) may be analysed at 87° C., when the rotation of invert sugar has a zero value.

The left and right handed forms of active substances, *e.g.* sugars, can be separated by the action of micro-organisms such as yeast and moulds, which preferentially destroy one of the isomers. The isomers differ also in their behaviour with digestive enzymes of the animal body.

The explanation generally adopted is that the enzymes of fermentation and digestion are themselves asymmetric and attach themselves to one optical isomer, in virtue of spacial arrangements which have been compared to the fitting of a key in a lock.

"The first step in what may prove to be an inquiry of considerable significance in biology is marked by the preparations of d- and l- forms of simple dyes containing an asymmetric system. The work has not proceeded far, but evidence has already been obtained that these optical isomerides are selectively absorbed by wool, and the prospect is thus

opened out that they may ultimately be used in the staining of sections so as to reveal more completely the chemical constitutions of tissues. This field of research has not been explored by the chemist, and there is ample scope for future developments of great importance." [6]

The Polarimeter has been successfully used on several occasions for the measurement of avidity of inactive acids and bases with the aid of an active base or active acid. Rimbach & Hörsters [7] used this method for Methyl Alcohol solutions following Walker, who had used it in aqueous solutions.

It is of interest to note that very high specific rotations are shown by some Camphor derivatives, first studied by Forster; pp.—Bisimino-camphordiphenylamine has the specific rotation in Alcohol of 2875, probably the highest known specific rotation. It is more than 10 times the value given by Quinine and Cinchonine, and may be compared with well-known substances such as Camphor and Sugar, which have specific rotations of 54 and 66 respectively. [8]

A review of the scientific applications of the Polarimeter would require a treatise on Stereo-Chemistry (see, however, Professor Frankland's Presidential Address to the Chemical Society, 1912). A summary of some of the latest work on natural rotation appears in the Annual Reports of the Chemical Society, [9] and begins with the interesting remark that the taste of some optically active compounds is different from that of their optical antipodes.

Although the Polarimeter is a routine instrument in several of the most important industries, any extension of its usefulness in other directions would be welcome to chemists, for, like the Refractometer, it has the advantage that none of the material for analysis is altered or destroyed. An unexpected application of the Polarimeter has been described by C. R. Smith, [11] who studied the muta-rotation of Gelatine. He found that Gelatine of the highest strength approached a definite maximum value of muta-rotation. The rotation of Gelatine solutions is measured at 35°C. immediately after they have been prepared. They are then allowed to remain at 15°C. for 12 hours, when the maximum change in rotation will have occurred. The first value (Ventzke degrees), is subtracted from the second when by comparison with Smith's Tables its jelly strength is found. The strongest Gelatine he measured yielded the figure 25 as the result of the above subtraction.

Much work has been carried out on rotatory dispersion, but the remarkable results obtained still await a theoretical explanation. The theory

put forward by Lorentz & Livens in 1906 has recently been tested by Wetterfors [10] who finds straight line relationships for Camphor in Benzene and Toluene, but not for other solvents. The theory can, therefore, only claim qualitative results. [10]

The idea that the phenomena of anomalous rotatory dispersion might be connected with the presence of an absorption band in the visible or in the near ultra-violet has been subjected to experimental criticism by three German authors, [12] but no connection could be established between the absorption curves and the rotatory dispersions of a number of optically active substances. [12]

Technical use was made of rotatory dispersion by M. E. Darmois in 1910,[13] who found that the proportions of alpha and beta Pinene in rectified Oil of Turpentine could be determined by measuring the rotatory dispersion.

Rolfe has described the general use of the Polarimeter in chemical analysis.[14]

Particulars of polarimeters for measuring rotatory dispersion, and some of the chief modern applications can be forwarded on application. The special polarimeters made by us for rotatory dispersion are equally useful for ordinary polarimetric work, differing from the former only in the addition of apparatus for the production of a spectrum.

Among the more recent applications of polarimetry in medicine may be mentioned, even if its value is disputed, the interesting study of the protective measures of the animal organism. " Die Diagnose der Schwangerschaft bei Mensch und Tier." Abderhalden, *Bioch. Arbeitsmethoden*, vol. 6, pp. 223-226.

The following papers are important for bio-chemists : " The Developments of micro-polarisation," by Emil Fischer, Abderhalden, *Bioch. Arbeitsmethoden*, vol. 5, p. 572 ; also E. Fischer, " Synthese von Polypeptiden," Sitzungsber. der Berliner Akademie (1908), 552 ; cf. Chem. Zentralblatt (1908), **2**, 315 ; see also concerning Mikropolarisation, Berichte, (1911), **44**, 129. (*Fischer, by the employment of small tubes, was able to measure the polarisation of volumes as small as* 0.1 *c.c.*)

Studying Biological Processes.

The instrument has also been used for studying biological processes, in which case it has been useful in detecting changes which would otherwise escape observation. For instance, Abderhalden found that the serum of normal dogs retained its original rotation if preserved at 37° C.

A change was only observed in cases of illness, particularly in the fevers due to infection. If a foreign protein or peptone was dissolved in a normal serum the original rotation of the mixture remains unaltered. Quite different results, however, were obtained with the serum of dogs which have been injected (subcutaneously, intravenously, etc.) with foreign protein or peptone. If such serum is mixed with protein, the mixture has no longer a constant rotation. Peptone formation was proved by dialysis, and thus the breakdown of protein by ferments contained in this serum or activated by the treatment was established. The detection of ferments not present or not active in the normal serum may be of great importance, although the numerical rotations measured may be of secondary interest. (Abderhalden, *Bioch. Arbeitsmethoden*, vol. 5, p. 575.)

The applications of the polarimeter to the study of the action of ferments is also interesting. (See " Methods of Studying the Action of Ferments," by L. Michaelis, Abderhalden, vol. 3, pp. 32-35.)

The above observations have been given as they may be the forerunners of new applications of the polarimeter in medical research.

The contents of the following extract should be present to the minds of all those working in polarimetry.

" Considerable confusion has been introduced into the subject of optical rotation by the fact that chemists, in their use of the polarimeter for the determination of the rotation of the plane of polarisation by optically active substances (chiefly liquids or solids in solution, but occasionally the solids themselves), have adopted a different convention, as regards the sign of the rotation, to that employed by physicists and crystallographers, who refer to the actual occurrence in the crystal itself. For instance, the right-handed quartz of the crystallographer actually rotates the plane of polarisation of light in the opposite direction to the so-called dextro-camphor of the chemist. The latter regards a rotation as right-handed or dextro when it appears clockwise to the observer looking through the eyepiece of the polarimeter. But the crystallographer regards himself as travelling with the beam of light, that is, as looking along the direction of propagation of the light ; if the movement of the light in the crystal is like that of a right-handed screw, clockwise, the crystal is right-handed or dextro-gyratory, and if the light moves in left-handed screw fashion, anti-clockwise, the crystal is læavo-rotatory or left-handed. It is very important that this should be quite clear." [15]

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SECTION V

APPLICATIONS OF X-RAY SPECTROGRAPHY AND CRYSTALLOGRAPHY TO METALLURGY AND TO CHEMICAL PROBLEMS

INTRODUCTION

The numbers descriptive of instruments refer to the publishers' catalogue of scientific instruments.

Varieties of X-rays.

It has long been known that an X-ray bulb emits rays of different quality as measured by the amount absorbed in passing through a sheet of metal. The more penetrating rays have been called " hard " and the less penetrating " soft," but although such terms are loose and indefinite they are convenient as relative indications of wavelength, the harder rays being those of shorter wavelength. Barkla found that such a mixed beam of X-rays falling upon a metal plate caused it to emit, in general, two beams of homogeneous rays, the one being very much harder or more penetrating than the other, and that these beams were characteristic of the material of the metal plate. It is essential for the production of characteristic rays that the exciting rays should be harder than the emitted rays. Soon afterwards, Kaye showed that the characteristic rays were emitted when the material in question formed the anticathode of a discharge tube. Barkla called these rays the K- and L-radiations.

Adopting Bragg's suggestion that a crystal should be used for reflection, Moseley was able to show that the K-radiation consisted of two different wavelengths forming sharp spectrum lines, one line, the softer ($K\alpha$) being more intense in each case, and that the wavelengths are distinctive of the emitting substance. Later Siegbahn showed that the $K\alpha$ line was a close doublet, and that in addition to the $K\beta$ line there was also a fainter, $K\gamma$, of still shorter wavelength.

Moseley recognised four lines in the *L* spectrum of an element, but it has been subsequently shown that there is a larger number of lines. Largely as the result of the work of Siegbahn and his collaborators, fairly comprehensive tables are available, giving carefully measured values of the wavelengths of radiations of both series, and in a number of cases also of a much softer series known as the *M*-series. In addition to the wavelengths characteristic of the anticathode, there is a quantity of " white " radiation, *i.e.* a region of continuously varying wavelength which is sharply bounded at the short wavelength end. The mean " hardness " of the radiation from an X-ray tube depends almost entirely on the value of the shortest wavelength emitted, and this depends on the *effective* voltage applied to the tube. The *intensity of radiation* is dependent upon the kind of tube used and the method of exciting it.

The Kind of Information Obtainable by the X-ray Spectrograph.

A general outline of the various methods of X-ray spectrography and crystallography, with bibliography, and a description of apparatus wherewith the most valuable of those methods can be carried out, will be found in the brochure issued by Adam Hilger Ltd., entitled " Dr. Müller's Universal X-ray Spectrograph."

In the present booklet, dealing as it does with applications only, a few words on the varieties of photographic record obtainable with X-ray spectrographs must suffice.

X-rays are produced by a high tension discharge (*e.g.* 60,000 volts) from a cathode, which discharge, impinging on a solid body (usually metal) which is called the " target " or " anticathode," results in radiations from the latter characteristic of the elements present at the surface thereof. These X-rays falling on a crystal are diffracted in certain definite directions depending on the wavelength of the rays, the nature of the crystal, and on the orientation of the latter relative to the incident rays.

X-rays and light are radiations of the same kind, except that the former are of much shorter wavelengths ; and the meaning of the word spectrum when used in connection with either radiation is the same. Radiations are so dealt with by an ordinary spectrograph that light of mixed wavelengths is arranged and photographically recorded in a series of lines or bands in order of the wavelengths of the component radiations. This is precisely what is done by an X-ray spectrograph except that the wavelengths concerned are very much shorter.

To such a photographic record is quite naturally applied the phrase X-ray spectrogram.

It is a characteristic feature of X-ray spectrography that *heterogeneous* X-rays are employed (X-rays, that is, of a variety of wavelengths). These are arranged and recorded by the apparatus in the order of their wavelengths, and such a record forms a means whereby the wavelengths of the component radiations can be found, when a crystal of known spacing is used.

Such X-ray spectra have the following advantages over those in the ordinary spectral regions :

(1) One spectral line of each element in the substance examined is stronger than any of the others and this line by itself suffices to identify the element ; so great is the dispersion in the X-ray region that discrimination between elements, even those which are immediate neighbours in the list of elements, is easy and certain.

(2) Non-metallic elements reveal their presence alike with metallic ones.

(3) The source consists of the substance to be analysed, preferably used in a special form of X-ray tube (F. 245), in which the anticathode is removable, so that the substance under test can be placed in position thereon.

There are two limitations to the range of elements that can be examined in this way. The wavelengths of the lighter elements may be so long (or according to the nomenclature of radiographers—so " soft ") as to be absorbed by the air. This applies to the 20 lightest elements (those in the series with the smallest atomic numbers).

The other limitation is that the heavier elements may give radiations of such short wavelengths that the characteristic radiations of the different elements are crowded together and not easily differentiated. Furthermore they may require voltages so high for the excitation of the characteristic rays that a suitable installation would be very expensive.

In the direction of the lighter elements the range can be increased by conducting the investigations *in vacuo*, but the increased complexity of the apparatus is not justified by such practical applications as those considered in this booklet.

All the elements in the series from scandium (atomic number 21) to platinum (atomic number 78) fall easily [1] within the limits of the very convenient Dr. Müller's X-ray Spectrograph (E. 45/6), and owing to the facilities for crystallography (see below) afforded by this instrument it

[1] " Easily "—that is by use of the most readily excited K-radiations. Intensities and exposures might be augmented to the point of exciting and recording the L-radiations of the whole of the elements heavier than caesium.

is not worth while to incur expense and sacrifice convenience in order to include a few more elements in the range for which spectrographic analysis can be employed.

X-ray Crystallography.

But X-ray spectrography as described above is only a small part of the work which can be done with X-ray spectrographs. The same class of instrument is usable in quite another way, the characteristic feature of which is the employment of *monochromatic* X-rays of known wavelength ; X-rays, that is, that consist of radiations of one wavelength.[1] Such rays falling on a crystal are diffracted in certain directions only.

One wavelength alone being used, the directions in which the rays are diverted now depend only on the nature of the crystal and its orientation—in short, on the arrangement of the atoms composing the crystal relative to the direction of the incident light.

The so diverted rays can be photographically recorded, and it is the records so obtained which have resulted during recent years in the measurement of the positions of the atoms in many crystals. For this kind of record it seems to us that another term is needed, and, failing more authoritative lead in the matter, we have adopted for it the phrase "X-ray Crystallogram."

From such crystallograms may be found the molecular structure of the substance as existing in the crystal.

It should here be pointed out that the word " crystal " has, in the light of X-ray investigations, acquired a greatly extended application. Many substances formerly regarded as amorphous, many liquids even, yield, under proper conditions, X-ray crystallograms from which their molecular structure can be deducted.

In the chemical applications of X-rays the determination of the structure of crystals is from the purely scientific point of view of preponderant importance, although the difficulties of performing such an analysis, being in many cases very great, have sufficed up till now to deter most chemical investigators from working in this field. But it is now beginning to be realised that there is a wide field of application in practical chemistry for an *empirical* use of X-ray crystallography. With the complete apparatus put on the market by the publishers of this booklet, it is neither difficult nor laborious to get good crystallograms.

[1] As described on page 57, the rays emitted from X-ray tubes are of mixed wavelength. Owing to the great intensity of the $K\alpha$ line the other lines, whether of the K or other series, can usually be ignored, while the " white " rays are never a source of confusion in this work. If desired, all radiations except the $K\beta$ which is usually needed for crystallography can be removed by using as a filter a thin sheet of the next lighter metal or of any salt of that metal.

whose value may be very great in the identification of chemical compounds, the quantitative analysis of mixtures difficult to separate by chemical means, and such like problems.

CHEMICAL AND METALLURGICAL APPLICATIONS—GENERAL

In addition, then, to their use in spectrum analysis, X-rays have furnished investigators with means of ascertaining directly the space-lattice structure of crystals and powders and of observing the orientation of the crystals forming the mass of a substance, when worked. Many metallurgical and chemical problems have been solved by the knowledge gained by investigators in this field. X-ray crystal analysis has enabled experimenters to throw light on phenomena relating to alloys, solid-solutions, allotropy, eutectic mixtures, ductility, and also to identify new constituents in agglomerates. It has enabled chemists to verify or disprove space formulae previously evolved by indirect methods.

As early as 1916, Jeffries, at a discussion on a paper read by Mathewson and Phillips on "The Recrystallisation of Cold-worked *Alpha* Brass on Annealing" (*Trans. Am. Inst. of Mining Engineers*, vol. 54, p. 608, 1916), said: "It seemed to me that Bragg's X-ray spectrometer might be used advantageously in determining the specific orientations, as well as in studying the changes of orientation during the recrystallisation period."

Since that time investigators have worked on these lines with the aid of the X-ray spectrometer, and Mathewson said in a paper read in Jan. 1925 (*Jour. Frank. Inst.*, vol. 199, p. 37, 1925): "It seems inevitable that the intelligent use of the X-ray spectrometer as an instrument for studying orientational changes will shortly reveal in its innermost mechanism the progression from one structural form to another in the process of cold working and recrystallisation, thus giving a quantitative picture of these important and baffling structural reorganisations."

Davey, in a paper outlining the methods used in applying X-ray crystal analysis to metallurgy (*Trans. Am. Soc. Steel Treating*, vol. 6, pp. 375-392, 1924), illustrated the utility of these methods by explaining how the arrangement of the atoms in metals gives a rational explanation of their relative ductilities and how the parameters of the crystal-lattices in a solid solution gives a rational picture of the mechanism of the solid solution.

At a discussion on one of the papers on the structure of iron read by Westgren and Phragmen (*Journ. Iron and Steel Inst.*, vol. 105, pp. 241-62, 1922), Sir W. Bragg said: "The handling of materials was practically in

the long run dependent upon the relations between the atomic forces that bound atom to atom. The most direct method of examining those forces depended on the solution of the structure of the crystal in which they were exerted, because the crystalline structure was the direct outcome and manifestation of the forces. The study of the crystal must lead straight into the heart of all accurate scientific work dealing with the materials handled in the iron and steel trade."

Sir W. Bragg on another occasion said (*Science*, vol. 60, p. 148, 1924): "With few exceptions every aspect of the behaviour of a solid substance depends on the mode of arrangement of its atoms and molecules. X-rays tell us directly (1) the number of molecules in the crystal unit cell, (2) their arrangement with such determinations of lengths and angles as are required to define the mode of arrangement in full, and (3) leaves us to ally our knowledge to all that we already possess."

Bain (*Ind. and Eng. Chem.*, vol. 16, p. 692, 1924), stated that: "The mechanism of solid solution was not known before X-rays were applied," and that X-ray examination led him to the conclusion that "Solution in the solid state takes place by the replacement of solvent atoms by solute atoms in the space-lattice of the solvent material."

In the same paper, Bain said that: "The pattern produced on the film in the crystallometer is as characteristic for a given crystal entity as a chemical test for an ion in the test-tube." He went on to state that: "In the case of mineralogic compounds not easily studied under the microscope, this method of study is helpful. The characteristic pattern can be recorded for a number of materials in a pure condition. Then, if there be a question as to whether new compounds, agglomerates, eutectics or solid solutions are formed from fusions of these materials, a study of the resultant film will yield a first approximation to the answer."

The scope and utility of X-ray crystal analysis as a practical means of assisting industrial metallurgists and chemists are already great and are being rapidly developed by able investigators. A brief indication of some of the recent applications and a list of summarised papers dealing with the more important work of an applied nature done with the aid of X-ray crystal analysis follows.

RECENT APPLICATIONS

1. "The chemist has, for example, come to the conclusion that the naphthalene molecule is a double benzene ring and the anthracene a triple benzene ring. The X-ray observations show that one of the sides of the

unit cell of the latter crystal is longer by 2·5 A.U. than the corresponding side of the other, all other dimensions of the two cells being very nearly the same. The width of the hexagonal ring in the diamond is 2·5 A.U., so that on the one hand the chemical evidence suggests that the length of the molecule is parallel to that edge of the two cells which shows differing values, and on the other hand the X-ray conclusions give material support to the chemical view." [1]

2. "Cobalt was thought to exist in two allotropic modifications. The X-rays have shown that the first form solidifying from the melt is of the hexagonal close-packed atomic system, and that the other form, as plated electrolytically from solution, is face-centered cubic like nickel."[2]

3. "Iron above 900° C. has such distinctly different properties from iron at, say, room temperature, that it was long considered to have a possible sharp allotropic modification. It was not until early in 1921, however, when the author (see also Westgren, *Chem. Met. Eng.*, vol. 25, p. 663, 1921) obtained characteristic films for the *gamma* and *alpha* modifications (high and low temperature forms respectively) of iron, that the exact nature of this allotropy of iron was known. The *gamma* iron was found to be face-centered cubic in form, while *alpha* iron is body-centered cubic. *Gamma* iron is therefore like nickel and copper, while *alpha* iron is like chromium and tungsten." [2]

4. "Since solid solution alters only the fundamental spacing of the solvent space-lattice, but never its type, it is evident that true continuous homogeneous series could never exist between pairs of metals of unlike crystalline type. Thus continuous solid solubility could not exist between nickel and chromium, copper and manganese and the like, although it has been customary to list them as such in works on metallography. With the knowledge obtained by X-ray studies of the nature of solid solutions, these series were immediately looked upon with suspicion, and investigation showed that at some concentrations they were not wholly of one crystalline type but composed of a mixture of both. Two kinds of solid solutions were found, *A* dissolved in *B* and *B* dissolved in *A*. Thus a real meaning is given to solvent and solute, the solvent metal being that one whose lattice is preserved." [2]

5. "The X-ray pattern gives a measure of the number of grains of a certain orientation present. In metals, in general, there is no predominant orientation; hence we have a measure of grain size." [2]

"The discovery of the extremely fine grained condition of martensite

[1] Sir W. Bragg, *Science*, vol. 60, p. 141, 1924.

[2] Bain, *Ind. and Eng. Chem.*, vol. 16, p. 692, 1924.

is thought to play an important part in the explanation of the causes of hardness " of steel.[1]

6. " The process of cold work has been found to develop new orientation in the crystal grains in spite of the fact that plastic deformation proceeds by translation of the crystal fragments along certain atomic planes of the grains. The X-rays have served to show just which planes provide easiest slip." [1]

7. " Another application of the grain size effect on the crystallograms was the identification of *beta* brass as a massive constituent at room temperature." [1]

8. " Another phenomenon has been observed by X-ray study. When this cold work is carried to a great degree in a single direction, the grain fragments tend to orientate themselves more and more nearly according to some geometric plan. This applies obviously to wire drawing and cold sheet rolling in particular. This effect becomes so marked in hard rolled sheet of some metals, that as far as X-ray diffraction for some planes is concerned, the sheet might well be considered to be a single crystal." [1]

9. Ammonium chloride and ammonium bromide have been shown to exist in two polymorphous modifications.[2]

10. Pure cobalt sometimes contains some face-centred cubic crystals, but usually crystallises in a hexagonal close-packed lattice. If traces of impurities are present, cobalt always crystallises in the face-centred cubic form, thus giving a rational explanation of the reason why impure cobalt is more ductile than the pure metal.[3]

11. X-ray crystal analysis has been used to confirm that the A_2 transformation in pure iron is not a change of phrase, and to show that there is no change of phrase below the A_3 point.[4]

12. In a paper describing The Distortion of an Aluminum Crystal during a Tensile Test, Taylor said: " Before the test contemplated could be carried out, it was necessary to enlist the help of an expert in crystal analysis by X-rays. Fortunately, Dr. Müller took up the work and succeeded in devising a satisfactory method of determining the orientation of the crystal axis." [5]

[1] See footnote 2 on page 61.

[2] Bartlett and Langmuir, *Journ. Am. Chem. Soc.*, vol. 43, p. 84, 1921.

[3] Hull, *Phys. Rev.*, vol. 17, p. 571, 1921.

[4] Kotaro Hondu, *Trans. Am. Soc. Steel Treating*, vol. 6, p. 187, 1924.

[5] Taylor and Elam, *Proc. Roy. Soc.* (Lond.), vol. 102, p. 643, 1922-23. Bakerian Lecture.

BIBLIOGRAPHY

Those interested in the details of the various applications to which X-ray crystal analysis has been put in recent years, will find a great many papers by distinguished investigators. Amongst the most illuminating are those read by Sir W. Bragg, W. L. Bragg, Gerlach, Hull and Davey, and by Polanyi and his collaborators, Weissenberg, Schmid, Mark and Ettisch. A list of these papers with a brief summary of their contents follows.

Author.	*Journal.*
W. L. Bragg.	*Phil. Mag.* (1920), **39**, 647-51. Determination of the structure of zinc oxide.
Hull.	*Phys. Rev.* (1921), **17**, 571-88. Structure of thirteen common metals determined.
Hull and Davey.	*Phys. Rev.* (1921), **17**, 549-70. Graphic method for determining the hexagonal and tetragonal crystal structure from X-ray data described.
Ettisch, Polanyi and Weissenberg.	*Physik. Zeit.* (1921), **22**, 646. Becker-Polanyi effect discovered for hard-drawn copper wire used for the quantitative determination of the crystal arrangement in hard drawn wires of W, Fe, Mo, Cu, Pd, Al and Ag.
Ettisch, Polanyi and Weissenberg.	*Zeit. Phys. Chem.* (1921), **99**, 332-7. A similar examination to the above for determining the fibrous structure of hard-drawn metals.
Gerlach.	*Physik. Zeit.* (1921), **22**, 557-9. Determination of the crystal-lattice structure of the oxides of Mg, Ca, Sr, and Ba, and the calculation of their densities from the lattice dimensions.
Gerlach and Pauli.	*Zeit. Physik.* (1921), **7**, 116-23. The crystal structure of magnesium oxide is proved to be a face-centred cubic lattice of the NaCl type.
Polanyi.	*Naturwissenschaften* (1922), **10**, 411-6. Röntgenographic investigation of crystal-lattice orientation during straining.
Mark, Polanyi and Schmid.	*Zeit. Physik.* (1922), **12**, 58. Investigation of the planes of slip of crystals during working of metals.

Author.	*Journal.*
KIRCHNER.	*Physik. Zeit.* (1922), **23**, 114. Note on Gerlach's paper above.
POLANYI.	*Zeit. Electrochem.* (1922), **28**, 16-20. Resumé of previous work.
W. L. BRAGG.	*Nature* (1923), **111**, Supplement III.-X. June. Lecture illustrating the use of X-rays for ascertaining crystal structure, particularly of carbon and organic compounds, with practical application to the explanation of their properties, such as strength, elasticity of materials, power of conducting electricity and heat, and other electrical and optical properties.
POLANYI.	*Zeit. Physik.* (1923), **17**, 42-53. Discussion of structure changes which take place when a metal is drawn into wire or rolled into foil. The fibrous structure produced in the former manner can be explained on the plausible assumption that slipping takes place with greatest ease when the angle between the direction of the force and that of the slip is greater than 45°.
MARK, POLANYI AND SCHMID.	*Naturwissenschaften* (1923), **11**, 256. Investigation of uni-crystalline wires of tin.
MARK, POLANYI AND SCHMID.	*Zeit. Physik.* (1923), **12**, 58-72, 78-110, 111-116. In the case of the technically important metals Fe, Cu, Al, W, Mg, Au, etc., it is shown that stretching orientation is not an important factor of tenacity, and that fibre structure has little bearing on it.
W. H. BRAGG.	*Nature* (1923), **111**, 532. Crystal structure of basic beryllium acetate shown to be that of a perfect tetrahedron.
MARK AND WEISSENBERG.	*Zeit. Physik.* (1923), **14**, 328-41. Investigation of structure of rolled metal foils.
MARK AND WEISSENBERG.	*Zeit. Physik.* (1923), **16**, 314-8. Two independent groups of space-lattice found in rolled foils of Ag, Al, Au, Cu, and Pt.
DAVEY.	*Phys. Rev.* (1923), **21**, 143-61. Precision measurements of crystals of the alkali halides.

Author.	*Journal.*
Mark and Weissenberg.	*Zeit. Physik.* (1923), **16**, 1-22. Röntgenographic determination of the structure of urea and tin tetraiodide. Only one space-lattice and one atomic arrangement for urea agrees with the X-ray data.
Mark and Weissenberg.	*Zeit. Physik.* (1923), **17**, 347-50. Crystal-lattice of triphenylmethane determined, and result obtained by Becker and Rose disproved. [See Becker and Rose, *Zeit. Physik.*, **17**, 351-2 (1923). Discrepancy explained by different crystal modifications.]
Mark and Polanyi.	*Zeit. Physik.* (1923), **18**, 75-96. Determination of space-lattice structure of white tin.
Gonell and Mark.	*Zeit. Phys. Chem.* (1923), **107**, 181-218. X-ray determination of structural formula of hexamethylenetetramine. Result agrees with Duden and Scharff's formula arrived at by chemical considerations.
Davey.	*Phys. Rev.* (1923), **21**, 380. Crystal structure of Cuprous selenide found to be similar to that of CaF_2 and that of zinc selenide similar to that of ZnS. Densities of Cu_2Se and ZnSe calculated from X-ray data are 7·154 and 5·283 respectively.
W. L. Bragg.	*Proc. Roy. Soc.* (Lond.), (1924), **105**A, 16-39. Structure of aragonite determined and its relation to calcite and the carbonates of Sr, Ba, and Pb, with which it is isomorphous, discussed.
Polanyi, Schiebold and Weissenberg.	*Zeit. Physik.* (1924), **23**, 337-40. Development of the X-ray procedure for determining crystal structure by rotation of crystals.
Gerlach.	*Zeit. Anorg. allgem. Chem.* (1924), **137**, 331-2. X-ray powder photographs made of diamond, graphite, charcoal and carbonado or "black-diamond," and conclusions drawn as to the structure of "black-diamond."

Author.	*Journal.*
Mark and Polanyi.	*Zeit. Physik.* (1924), **22**, 200. The crystal lattice structure of the two tins.

Rolling and Annealing of Metals

Other papers of a most instructive character, adding further information on the various problems dealt with, have also been contributed by other investigators.

The following references are to papers devoted to the observation of metals during rolling and annealing.

Author.	*Journal.*
Nishikawa Asahara.	*Phys. Rev.* (1920), **15**, 38-45. Beam of heterogeneous rays passed through sheet of metal and pattern photographed.
Niwa and Matûra.	*Researches Electro. Tech. Lab.*, Tokyo, Japan (1922), **122**, 1-20. (*Science Abstracts*, **27**A 53.) X-ray investigation of the effect of cold-rolling a sheet-metal.
Thomassen.	*Zeit. Metallkunde* (1923), **15**, 306. Investigation of the crystal structure of the surface layer of worked metals.
Wever.	*Zeit. Physik.* (1924), **28**, 69-90. Study of the progressive changes of large Al crystals as they are cold-rolled.

Investigations Concerning Alloys

The following references show how the methods of X-ray crystal analysis have been used to elucidate problems connected with alloys.

Author.	*Journal.*
Fuller.	*Gen. Elect. Rev.* (1922), **25**, 746-50. X-ray determination of the composition of alloys (Cu-Zu alloy used). The fact that no destruction of the material is necessary is emphasized.
Becker.	*Zeit. Metallkunde* (1923), **15**, 303-5. Review of present knowledge of crystal structure and a table showing the systems in which 39 metals crystallise.

Author.	*Journal.*
Owen and Preston.	*Proc. Phys. Soc.* (Lond.), (1923), **36**, 14-30. X-ray analysis of solid solution of Al-Cu, Al-Mg, and Cu-Ni. In each case the solute atom replaces an atom in the lattice of the solvent, the substitution being accompanied by distortion of the lattice.
Owen and Preston.	*Proc. Phys. Soc.* (Lond.), (1923), **36**, 49-66. X-ray analysis of zinc-copper alloys.

The following list gives recent papers of general metallurgical interest.

Author.	*Journal.*
Burger.	*Physica* (1922), **2**, 114. X-ray determination of density of tungsten.
McKeehan and Cioffi.	*Phys. Rev.* (1922), **19**, 444-6. X-ray determination of crystal structure and density of solid mercury. Found to have simple rhombohedral lattice. Density by X-ray data, 13·97. Density by Mallet 14·193, and by Dewar 14·382.
Van Arkel.	*Physica* (1923), **3**, 76-87. Uni-crystalline tungsten used to explain why mechanical properties depend on the orientation of the crystals.
Dickenson and Pauling.	*Journ. Am. Chem. Soc.* (1923), **45**, 1466-71. Determination of crystal structure of molybdenite.
McKeehan.	*Phys. Rev.* (1923), **21**, 503-8. Determination of crystal structure of quartz.
Mauguin.	*Compt. Rend.* (1923), **176**, 1331-4. The reflection of X-rays by certain unusual lattice planes of calcite.
Pauling.	*Journ. Am. Chem. Soc.* (1923), **45**, 2777-80. Magnesium stannide shown to have same type of crystal structure as CaF_2.
St. John.	*Phys. Rev.* (1923), **21**, 389. Determination of crystal structure of manganese dioxide. Polianite shown to have same crystal pattern as pyrolusite. Crystallographic classification of pyrolusite as orthorhombic is therefore due to pseudomorphism.

Author.	*Journal.*
Bayley.	*Phys. Rev.* (1923), **21**, 716. Effect of X-rays on halite and sylvite. Short exposure to X-rays makes easy separation possible owing to colour changes produced.
Zorning.	*Army Ordnance* (1923), **4**, 77-83. Examination of steel by X-rays. Various conclusions drawn as to the structure and composition of the various conditions of 1·10 % carbon steel.
Glocker, Berthold, and Neeff.	*Naturwissenschaften* (1924), **12**, 86-7. Advances of X-ray investigation of thick masses of metal by the use of a moving diaphragm. A rotating diaphragm made of a spiral of tin band was used and a groove 0·3 mm. deep on the further side of a block of aluminium 10 cm. thick could be detected. Without the diaphragm, a groove under 1·0 mm. was invisible.
Ott.	*Zeit. Physik.* (1924), **22**, 201-14. Determination of the lattice structure of aluminium nitride by Laue photographs.
Westgren and Phragmen.	*Journ. Iron and Steel Inst.* (1924), **109**, 159. X-ray studies on the crystal structure of steel. A pure δ iron X-ray interference photograph from Fe at 1450° proves that this phase has same structure as α iron. Lattice dimensions of austenite increase in size with rising carbon content. This solid solution is not formed by simple substitution of metal atoms by carbon atoms, but is an additive product. The carbon atoms are situated in the interstices between the metal atoms, which latter alone occupy the points of the face-centred cubic lattice.
Williams.	*Iron and Steel Inst., Carnegie Schol. Memoirs* (1924). **13**, 175-95. X-ray analysis used to study hardened steel. Laue's and Bragg's methods used.

Various Chemical Problems

The following papers show applications of X-ray crystal analysis to a variety of chemical problems.

Author.	*Journal.*
James and Turnstall.	*Phil. Mag.* (1920), **40**, 233-40. Determination of the crystal structure of antimony.
Dauvillier.	*Compt. Rend.* (1920), **171**, 627-9. Discussion of the mechanism of chemical reaction promoted by X-rays.
Ogg.	*Phil. Mag.* (1921), **42**, 163-6. Determination of the crystal structure of antimony and bismuth.
James.	*Phil. Mag.* (1921), **42**, 193-6. Determination of the crystal structure of bismuth.
Becker and Jancke.	*Zeit. Phys. Chem.* (1921), **99**, 242-74. Spectrograms and parameters of 23 lithium salts of fatty acids and free fatty acids and of 24 other organic compounds determined. The parameters so found are in agreement in most cases with those found by goniometric measurements.
Nabuo Yamada.	*Journ. Chem. Soc.* (Japan), (1923), **44**, 210-9. X-ray analysis of stannic oxide. Causes of the existence of the α and β forms of H_2SnO_3 investigated by preparing the oxide by various methods and comparing them with natural cassiterite by means of X-ray photographs, using Debye and Scherrer's method.
Müller.	*Journ. Chem. Soc.* (1923), **123**, 2043-7. X-ray investigation of the fatty acids. The long CH_2 chains in the molecules of paraffin-wax could be detected by X-rays. Photographs of the reflection lines obtained with capric, lauric, myristic, palmitic, stearic and behenic acids were taken. The spacings existing in these acids increase as the length of the number of CH_2 groups increases.

Author.	*Journal.*
Broomè.	*Physik. Zeit.* (1923), **24**, 124-30. X-ray observations on solid benzene.
Wyckoff.	*Am. Journ. Science* (1923), **5**, 209-17. Investigation of the crystal structure of the alums.
Kolkmeijer, Bijvoet and Karssen.	*Zeit. Physik.* (1923), **14**, 291-5. Investigation of crystal structure of sodium bromate and sodium chloride and comparison of results obtained with those obtained by other methods.
Bozorth.	*Journ. Am. Chem. Soc.* (1923), **45**, 2128-35. Determination of the crystal structure of potassium hydrogen fluoride.
Schwarz and Klingenfuss.	*Zeit. Electrochem.* (1923), **29**, 470-4. Investigation of the nature of the action of X-rays on contact platinum with reference to the manufacture of sulphuric acid.
Bijvoet.	*Rec. Trav. Chim.* (1923), **42**, 859-903. X-ray investigation of the crystal structure of lithium and lithium hydride.
Karssen.	*Rec. Trav. Chim.* (1923), **42**, 904-30. X-ray investigation of the crystal structure of sodium bromate and sodium chloride.
Yardley.	*Proc. Roy. Soc.* (Lond.), (1924), **105**A, 451-67. Investigation of the crystal structure of succinic acid, succinic anhydride and succinimide.
Bradley.	*Phil. Mag.* (1924), **47**, 657-70. Determination of the crystal structure of metallic arsenic, which is shown to have a structure similar to that of antimony and bismuth. The X-ray measurements agree with the crystallographic calculations.
Pauling and Dickenson.	*Journ. Am. Chem. Soc.* (1924), **46**, 1615-22. Structure of crystals of uranyl nitrate hexahydrate investigated.
Levi.	*Giorn. Chim. Ind. App.* (1924), **6**, 333-4. Crystal structure of calcium hydroxide shown to be similar to that of magnesium hydroxide.

Author.	*Journal.*
Bradley.	*Phil. Mag.* (1924), **48**, 477-96. Crystal structures of rhombohedral forms of selenium and tellurium found to be of a three-fold spiral form composed of three interpenetrating simple triangular lattices allowing of two enantiomorphous forms indistinguishable by the methods of X-ray crystal analysis.

Work on Fibres

X-rays have further been usefully applied to the investigation of problems connected with the structure, chemical constitution, and mechanical properties of organic fibres. Systematic work of this nature has been done by Polanyi and his associates, a list of whose papers follows.

Author.	*Journal.*
Debye and Scherrer.	*Physik. Zeit.* (1917), **18**, 291-301. Discussion of X-ray interference produced by irregularly orientated particles.
Herzog and Jancke.	*Zeit. Physik.* (1920), **3**, 196-8. X-ray spectroscopic methods used to show that cellulose obtained from various sources has the same crystal structure.
Herzog, Jancke and Polanyi.	*Zeit. Physik.* (1920), **3**, 343-8. Investigation of cellulose by X-rays. Discussion of the interference diagrams obtained with a bundle of parallel cellulose fibres.
Polanyi.	*Naturwissenschaften* (1921), **9**, 288 and 337. Chemical constitution of cellulose deduced from X-ray determination of its crystal structure. Silk also investigated.
Polanyi.	*Zeit. Physik.* (1921), **7**, 149-80. Theoretical paper dealing with the optics of the reflection of monochromatic X-rays from crystal particles.
Polanyi and Weissenberg.	*Zeit. Physik.* (1922), **9**, 123-63. Determination of crystal structure from the Röntgenographs of fibres.

Author.	*Journal.*
Polanyi and Weissenberg.	*Zeit. Physik.* (1922), **10**, 44-53. Further development of above paper.
Polanyi, Herzog and Jancke.	*Zeit. Physik.* (1924), **20**, 413. Investigation of the structure of cellulose and silk.
Ganell.	*Zeit. Physik.* (1924), **25**, 118-20. X-ray spectrographic observations on cellulose.

LIST OF COGNATE PUBLICATIONS

The following further printed matter on the subject dealt with in this book may be obtained on application to Adam Hilger, Limited, 24 Rochester Place, Camden Road, London, N.W. 1; post free except otherwise mentioned.

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Spectrum Analysis in an Industrial Laboratory. W. H. Bassett and C. H. Davis. Reprint from *Trans. Amer. Inst. of Mining and Metallurgical Engineers*, read Feb. 1922, price 7d. post free.

Spectrum Analysis with Hilger Instruments. Royal 8vo. Pp. 23. Paper bound. 9d. nett. 10d. post free.

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